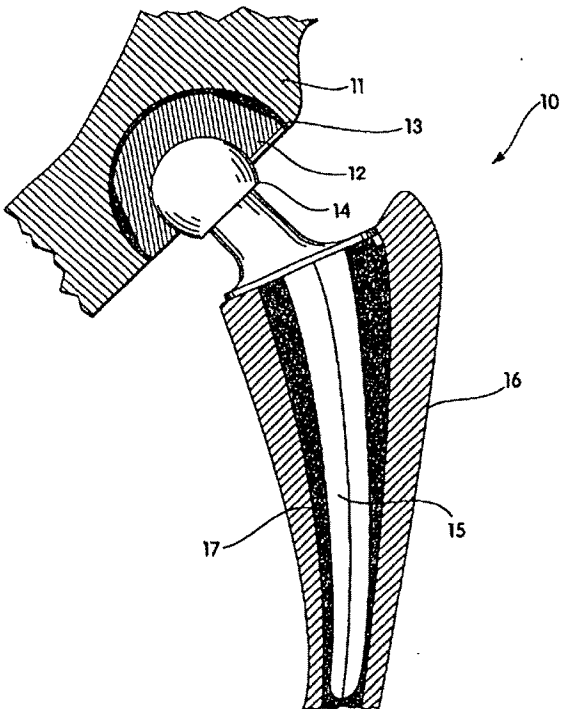


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(54) Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE PROSTHETIC DEVICES			
(57) Abstract			
<p>A medical prosthesis for use within the body which is formed of radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals, is described. Preferred prostheses exhibit reduced production of particles from the prosthesis during wear of the prosthesis, and are substantially oxidation resistant. Methods of manufacture of such devices and material used therein are also provided.</p>			
			

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**RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT
POLYETHYLENE PROSTHETIC DEVICES**

This application is a continuation-in-part of application
5 Serial No. 08/726,313, filed on October 2, 1996, entitled
RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT
POLYETHYLENE PROSTHETIC DEVICES, which is a continuation-in-part
of application Serial Number 08/600,744, filed on February 13,
1996, entitled MELT-IRRADIATED ULTRA HIGH MOLECULAR WEIGHT
10 POLYETHYLENE PROSTHETIC DEVICES. The entire contents of the
parent applications are expressly incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to the orthopedic field and
the provision of prostheses, such as hip and knee implants, as
15 well as methods of manufacture of such devices and material used
therein.

BACKGROUND OF THE INVENTION

The use of synthetic polymers, e.g., ultra high molecular
weight polyethylene, with metallic alloys has revolutionized the
20 field of prosthetic implants, e.g., their use in total joint
replacements for the hip or knee. Wear of the synthetic polymer
against the metal of the articulation, however, can result in
severe adverse effects which predominantly manifest after
several years. Various studies have concluded that such wear
25 can lead to the liberation of ultrafine particles of
polyethylene into the periprosthetic tissues. It has been
suggested that the abrasion stretches the chain folded
crystallites to form anisotropic fibrillar structures at the
articulating surface. The stretched-out fibrils can then
30 rupture, leading to production of submicron sized particles. In
response to the progressive ingress of these polyethylene
particles between the prosthesis and bone, macrophage-induced
resorption of the periprosthetic bone is initiated. The
macrophage, often being unable to digest these polyethylene
35 particles, synthesize and release large numbers of cytokines and
growth factors which can ultimately result in bone resorption by
osteoclasts and monocytes. This osteolysis can contribute to
mechanical loosening of the prosthesis components, thereby
sometimes requiring revision surgery with its concomitant
40 problems.

Summary of the Invention

It is an object of the invention to provide an implantable prosthesis device formed at least in part of radiation treated ultra high molecular weight polyethylene (UHMWPE) having no detectable free radicals, so as to reduce production of fine particles from the prosthesis during wear of the prosthesis.

It is another object of the invention to reduce osteolysis and inflammatory reactions resulting from prosthesis implants.

It is yet another object of the invention to provide a prosthesis which can remain implanted within a person for prolonged periods of time.

It is yet another object of the invention to provide improved UHMWPE which can be used in the prostheses of the preceding objects and/or in other fabricated articles.

Still another object of the invention is to provide improved UHMWPE which has a high density of cross-links and no detectable free radicals.

A still further object of the invention is to provide improved UHMWPE which has improved wear resistance.

According to the invention, a medical prosthesis for use within the body which is formed of radiation treated ultra high molecular weight polyethylene (UHMWPE) having substantially no detectable free radicals, is provided. The radiation can be, e.g., gamma or electron radiation. The UHMWPE has a cross-linked structure. Preferably, the UHMWPE is substantially not oxidized and is substantially oxidation resistant.

Variations include, e.g., the UHMWPE having three melting peaks, two melting peaks or one melting peak. In certain embodiments, the UHMWPE has a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus, so as to reduce production of fine particles from the prosthesis during wear of the prosthesis. Part of the prosthesis can be, e.g., in the form of a cup or tray shaped article having a load bearing surface made of this UHMWPE. This load bearing surface can be in contact with a second part of the prosthesis having a mating load bearing surface of a metallic or ceramic material.

Another aspect of the invention is radiation treated UHMWPE

having substantially no detectable free radicals. This UHMWPE has a cross-linked structure. Preferably, this UHMWPE is substantially not oxidized and is substantially oxidation resistant. Variations include, e.g., the UHMWPE having three
5 melting peaks, two melting peaks or one melting peak.

Other aspects of the invention are fabricated articles, e.g., with a load bearing surface, and wear resistant coatings, made from such UHMWPE. One embodiment is where the fabricated article is in the form of a bar stock which is capable of being
10 shaped into articles by conventional methods, e.g., machining.

Yet another aspect of the invention includes a method for making a cross-linked UHMWPE having substantially no detectable free radicals. Conventional UHMWPE having polymeric chains is provided. This UHMWPE is irradiated so as to cross-link said
15 polymeric chains. The UHMWPE is heated above the melting temperature of the UHMWPE so that there are substantially no detectable free radicals in the UHMWPE. The UHMWPE is then cooled to room temperature. In certain embodiments, the cooled UHMWPE is machined and/or sterilized.

20 One preferred embodiment of this method is called CIR-SM, i.e., cold irradiation and subsequent melting. The UHMWPE that is provided is at room temperature or below room temperature.

Another preferred embodiment of this method is called WIR-SM, i.e., warm irradiation and subsequent melting. The
25 UHMWPE that is provided is pre-heated to a temperature below the melting temperature of the UHMWPE.

Another preferred embodiment of this method is called WIR-AM, i.e., warm irradiation and adiabatic melting. In this embodiment, the UHMWPE that is provided is pre-heated to a
30 temperature below the melting temperature of the UHMWPE, preferably between about 100°C to below the melting temperature of the UHMWPE. Preferably, the UHMWPE is in an insulating material so as to reduce heat loss from the UHMWPE during processing. The pre-heated UHMWPE is then irradiated to a high
35 enough total dose and at a fast enough dose rate so as to generate enough heat in the polymer to melt substantially all the crystals in the material and thus ensure elimination of substantially all detectable free radicals generated by, e.g., the irradiating step. It is preferred that the irradiating step

use electron irradiation so as to generate such adiabatic heating.

Another aspect of this invention is the product made in accordance with the above described method.

5 Yet another aspect of this invention, called MIR, i.e., melt irradiation, is a method for making crosslinked UHMWPE. Conventional UHMWPE is provided. Preferably, the UHMWPE is surrounded with an inert material that is substantially free of oxygen. The UHMWPE is heated above the melting temperature of
10 the UHMWPE so as to completely melt all crystalline structure. The heated UHMWPE is irradiated, and the irradiated UHMWPE is cooled to about 25°C.

In an embodiment of MIR, highly entangled and crosslinked UHMWPE is made. Conventional UHMWPE is provided. Preferably,
15 the UHMWPE is surrounded with an inert material that is substantially free of oxygen. The UHMWPE is heated above the melting temperature of the UHMWPE for a time sufficient to enable the formation of entangled polymer chains in the UHMWPE. The heated UHMWPE is irradiated so as to trap the polymer chains
20 in the entangled state, and the irradiated UHMWPE is cooled to about 25°C.

The invention also features a method of making a medical prosthesis from radiation treated UHMWPE having substantially no detectable free radicals, the prosthesis resulting in reduced
25 production of particles from the prosthesis during wear of the prosthesis. Radiation treated UHMWPE having no detectable free radicals is provided. A medical prosthesis is formed from this UHMWPE so as to reduce production of particles from the prosthesis during wear of the prosthesis, the UHMWPE forming a
30 load bearing surface of the prosthesis. Formation of the prosthesis can be accomplished by standard procedures known to those skilled in the art, e.g., machining.

Also provided in this invention is a method of treating a body in need of a medical prosthesis. A shaped prosthesis
35 formed of radiation treated UHMWPE having substantially no detectable free radicals is provided. The prosthesis is applied to the body in need of the prosthesis. The prosthesis reduces production of particles from the prosthesis during wear of the prosthesis. In preferred embodiments, the UHMWPE forms a load

bearing surface of the prosthesis.

The above and other objects, features and advantages of the present invention will be better understood from the following specification when read in conjunction with the accompanying
5 drawings.

Brief Description of the Drawings

FIG. 1 is a cross-sectional view through the center of a medical hip joint prosthesis in accordance with a preferred
10 embodiment of this invention;

FIG. 2 is a side view of an acetabular cup liner as shown in FIG. 1;

FIG. 3 is a cross-sectional view through line 3-3 of FIG. 2;

15 FIG. 4 is a graph showing the crystallinity and melting point of melt-irradiated UHMWPE at different irradiation doses;

FIG. 5 is an environmental scanning electron micrograph of an etched surface of conventional UHMWPE showing its crystalline structure;

20 FIG. 6 is an environmental scanning electron micrograph of an etched surface of melt-irradiated UHMWPE showing its crystalline structure at approximately the same magnification as in FIG. 5; and

FIG. 7 is a graph showing the crystallinity and melting
25 point at different depths of a melt-irradiated UHMWPE cup.

FIG. 8 is a graph showing DSC melting endotherms for Hoechst-Celanese GUR 4050 UHMWPE prepared using warm irradiation and partial adiabatic melting (WIR-AM), with and without subsequent heating.

30 FIG. 9 is a graph showing DSC melting endotherms for Hoechst-Celanese GUR 1050 UHMWPE prepared using warm irradiation and partial adiabatic melting (WIR-AM), with and without subsequent heating.

FIG. 10 is a graph showing adiabatic heating of UHMWPE
35 treated by WIR-AM with a pre-heat temperature of 130°C.

FIG. 11 is a graph showing tensile deformation behavior of unirradiated UHMWPE, CIR-SM treated UHMWPE, and WIR-AM treated UHMWPE.

Detailed Description

This invention provides a medical prosthesis for use within the body which is formed of radiation treated ultra high molecular weight polyethylene (UHMWPE) which has substantially
5 no detectable free radicals.

A medical prosthesis in the form of a hip joint prosthesis is generally illustrated at 10 in FIG. 1. The prosthesis shown has a conventional ball head 14 connected by a neck portion to a stem 15 which is mounted by conventional cement 17 to the femur
10 16. The ball head can be of conventional design and formed of stainless steel or other alloys as known in the art. The radius of the ball head closely conforms to the inner cup radius of an acetabular cup 12 which can be mounted in cement 13 directly to the pelvis 11. Alternatively, a metallic acetabular shell can
15 be cemented to the pelvis 11 and the acetabular cup 12 can form a coating or liner connected to the metallic acetabular shell by means as are known in the art.

The specific form of the prosthesis can vary greatly as known in the art. Many hip joint constructions are known and
20 other prostheses such as knee joints, shoulder joints, ankle joints, elbow joints and finger joints are known. All such prior art prostheses can be benefited by making at least one load bearing surface of such prosthesis of a high molecular weight polyethylene material in accordance with this invention.
25 Such load bearing surfaces can be in the form of layers, linings or actual whole devices as shown in FIG. 1. In all cases, it is preferred that the load bearing surface act in conjunction with a metallic or ceramic mating member of the prosthesis so that a sliding surface is formed therebetween. Such sliding surfaces
30 are subject to breakdown of the polyethylene as known in the prior art. Such breakdown can be greatly diminished by use of the materials of the present invention.

FIG. 2 shows the acetabular cup 12 in the form of a half hollow ball-shaped device better seen in the cross-section of
35 FIG. 3. As previously described, the outer surface 20 of the acetabular cup need not be circular or hemispherical but can be square or of any configuration to be adhered directly to the pelvis or to the pelvis through a metallic shell as known in the art. The radius of the acetabular cup shown at 21 in FIG. 3 of

the preferred embodiment ranges from about 20 mm to about 35 mm. The thickness of the acetabular cup from its generally hemispherical hollow portion to the outer surface 20 is preferably about 8 mm. The outer radius is preferably in the
5 order of about 20 mm to about 35 mm.

In some cases, the ball joint can be made of the UHMWPE of this invention and the acetabular cup formed of metal, although it is preferred to make the acetabular cup or acetabular cup liner of UHMWPE to mate with the metallic ball. The particular
10 method of attachment of the components of the prosthesis to the bones of the body can vary greatly as known in the art.

The medical prosthesis of this invention is meant to include whole prosthetic devices or portions thereof, e.g., a component, layer or lining. The medical prosthesis includes,
15 e.g., orthopedic joint and bone replacement parts, e.g., hip, knee, shoulder, elbow, ankle or finger replacements. The prosthesis can be in the form, e.g., of a cup or tray shaped article which has a load bearing surface. Other forms known to those skilled in the art are also included in the invention.
20 Medical prostheses are also meant to include any wearing surface of a prosthesis, e.g., a coating on a surface of a prosthesis in which the prosthesis is made from a material other than the UHMWPE of this invention.

The prostheses of this invention are useful for contact
25 with metal containing parts formed of, e.g., cobalt chromium alloy, stainless steel, titanium alloy or nickel cobalt alloy, or with ceramic containing parts. For example, a hip joint is constructed in which a cup shaped article having an inner radius of 25 mm, is contacted with a metal ball having an outer radius
30 of 25 mm, so as to closely mate with the cup shaped article. The load bearing surface of the cup shaped article of this example is made from the UHMWPE of this invention, preferably having a thickness of at least about 1 mm, more preferably having a thickness of at least about 2 mm, more preferably
35 having a thickness of at least about $\frac{1}{4}$ inch, and more preferably yet having a thickness of at least about $\frac{1}{3}$ inch.

The prostheses can have any standard known form, shape, or configuration, or be a custom design, but have at least one load bearing surface of UHMWPE of this invention.

The prostheses of this invention are non-toxic to humans. They are not subject to deterioration by normal body constituents, e.g., blood or interstitial fluids. They are capable of being sterilized by standard means, including, e.g.,
5 heat or ethylene oxide.

By UHMWPE is meant linear non-branched chains of ethylene that have molecular weights in excess of about 500,000, preferably above about 1,000,000, and more preferably above about 2,000,000. Often the molecular weights can be at least as
10 high as about 8,000,000. By initial average molecular weight is meant the average molecular weight of the UHMWPE starting material, prior to any irradiation.

Conventional UHMWPE is standardly generated by Ziegler-Natta catalysis, and as the polymer chains are generated
15 from the surface catalytic site, they crystallize, and interlock as chain folded crystals. Examples of known UHMWPE powders include Hifax Grade 1900 polyethylene (obtained from Montell, Wilmington, Delaware), having a molecular weight of about 2 million g/mol and not containing any calcium stearate; GUR 4150,
20 also known as GUR 415, (obtained from Hoescht Celanese Corp., Houston, TX), having a molecular weight of about 4-5 million g/mol and containing 500 ppm of calcium stearate; GUR 4050 (obtained from Hoescht Celanese Corp., Houston, TX), having a molecular weight of about 4-5 million g/mol and not containing
25 any calcium stearate; GUR 4120 (obtained from Hoescht Celanese Corp., Houston, TX), having a molecular weight of about 2 million g/mol and containing 500 ppm of calcium stearate; GUR 4020 (obtained from Hoescht Celanese Corp., Houston, TX), having a molecular weight of about 2 million g/mol and not containing
30 any calcium stearate; GUR 1050 (obtained from Hoescht Celanese Corp., Germany), having a molecular weight of about 4-5 million g/mol and not containing any calcium stearate; GUR 1150 (obtained from Hoescht Celanese Corp., Germany), having a molecular weight of about 4-5 million g/mol and containing 500
35 ppm of calcium stearate; GUR 1020 (obtained from Hoescht Celanese Corp., Germany), having a molecular weight of about 2 million g/mol and not containing any calcium stearate; and GUR 1120 (obtained from Hoescht Celanese Corp., Germany), having a molecular weight of about 2 million g/mol and containing 500 ppm

of calcium stearate. Preferred UHMWPEs for medical applications are GUR 4150, GUR 1050 and GUR 1020. By resin is meant powder.

UHMWPE powder can be consolidated using a variety of different techniques, e.g., ram extrusion, compression molding or direct compression molding. In ram extrusion, the UHMWPE powder is pressurized through a heated barrel whereby it is consolidated into a rod stock, i.e., bar stock (can be obtained, e.g., from Westlake Plastics, Lenni, PA). In compression molding, the UHMWPE powder is consolidated under high pressure into a mold (can be obtained, e.g., from Poly-Hi Solidur, Fort Wayne, IN, or Perplas, Stanmore, U.K.). The shape of the mold can be, e.g., a thick sheet. Direct compression molding is preferably used to manufacture net shaped products, e.g., acetabular components or tibial knee inserts (can be obtained, e.g., from Zimmer, Inc., Warsaw, IN). In this technique, the UHMWPE powder is compressed directly into the final shape. "Hockey pucks", or pucks, are generally machined from ram extruded bar stock or from a compression molded sheet.

By radiation treated UHMWPE is meant UHMWPE which has been treated with radiation, e.g., gamma radiation or electron radiation, so as to induce cross-links between the polymeric chains of the UHMWPE.

By substantially no detectable free radicals is meant substantially no free radicals as measured by electron paramagnetic resonance, as described in Jahan et al., J. Biomedical Materials Research 25:1005 (1991). Free radicals include, e.g., unsaturated trans-vinylene free radicals. UHMWPE that has been irradiated below its melting point with ionizing radiation contains cross-links as well as long-lived trapped free radicals. These free radicals react with oxygen over the long-term and result in the embrittlement of the UHMWPE through oxidative degradation. An advantage of the UHMWPE and medical prostheses of this invention is that radiation treated UHMWPE is used which has no detectable free radicals. The free radicals can be eliminated by any method which gives this result, e.g., by heating the UHMWPE above its melting point such that substantially no residual crystalline structure remains. By eliminating the crystalline structure, the free radicals are able to recombine and thus are eliminated.

The UHMWPE which is used in this invention has a cross-linked structure. An advantage of having a cross-linked structure is that it will reduce production of particles from the prosthesis during wear of the prosthesis.

5 It is preferred that the UHMWPE be substantially not oxidized. By substantially not oxidized is meant that the ratio of the area under the carbonyl peak at 1740 cm^{-1} in the FTIR spectra to the area under the peak at 1460 cm^{-1} in the FTIR spectra of the cross-linked sample be of the same order of
10 magnitude as the ratio for the sample before cross-linking.

It is preferred that the UHMWPE be substantially oxidation resistant. By substantially oxidation resistant is meant that it remains substantially not oxidized for at least about 10 years. Preferably, it remains substantially not oxidized for at
15 least about 20 years, more preferably for at least about 30 years, more preferably yet for at least about 40 years, and most preferably for the entire lifetime of the patient.

In certain embodiments, the UHMWPE has three melting peaks. The first melting peak preferably is about 105°C to about 120°C ,
20 more preferably is about 110°C to about 120°C , and most preferably is about 118°C . The second melting peak preferably is about 125°C to about 140°C , more preferably is about 130°C to about 140°C , more preferably yet is about 135°C , and most preferably is about 137°C . The third melting peak preferably is
25 about 140°C to about 150°C , more preferably is about 140°C to about 145°C , and most preferably is about 144°C . In certain embodiments, the UHMWPE has two melting peaks. The first melting peak preferably is about 105°C to about 120°C , more preferably is about 110°C to about 120°C , and most preferably is
30 about 118°C . The second melting peak preferably is about 125°C to about 140°C , more preferably is about 130°C to about 140°C , more preferably yet is about 135°C , and most preferably is about 137°C . In certain embodiments, the UHMWPE has one melting peak. The melting peak preferably is about 125°C to about 140°C , more
35 preferably is about 130°C to about 140°C , more preferably yet is about 135°C , and most preferably is about 137°C . Preferably, the UHMWPE has two melting peaks. The number of melting peaks is determined by differential scanning calorimetry (DSC) at a heating rate of $10^{\circ}\text{C}/\text{min}$.

The polymeric structure of the UHMWPE used in the prostheses of this invention results in the reduction of production of UHMWPE particles from the prosthesis during wear of the prosthesis. As a result of the limited number of particles being shed into the body, the prosthesis exhibits longer implant life. Preferably, the prosthesis can remain implanted in the body for at least 10 years, more preferably for at least 20 years and most preferably for the entire lifetime of the patient.

The invention also includes other fabricated articles made from radiation treated UHMWPE having substantially no detectable free radicals. Preferably, the UHMWPE which is used for making the fabricated articles has a cross-linked structure. Preferably, the UHMWPE is substantially oxidation resistant. In certain embodiments, the UHMWPE has three melting peaks. In certain embodiments, the UHMWPE has two melting peaks. In certain embodiments, the UHMWPE has one melting peak. Preferably, the UHMWPE has two melting peaks. The fabricated articles include shaped articles and unshaped articles, including, e.g., machined objects, e.g., cups, gears, nuts, sled runners, bolts, fasteners, cables, pipes and the like, and bar stock, films, cylindrical bars, sheeting, panels, and fibers. Shaped articles can be made, e.g., by machining. The fabricated article can be, e.g., in the form of a bar stock which is capable of being shaped into a second article by machining. The fabricated articles are particularly suitable for load bearing applications, e.g., high wear resistance applications, e.g., as a load bearing surface, e.g., an articulating surface, and as metal replacement articles. Thin films or sheets of the UHMWPE of this invention can also be attached, e.g., with glue, onto supporting surfaces, and thus used as a wear resistant load bearing surface.

The invention also includes radiation treated UHMWPE which has substantially no detectable free radicals. The UHMWPE has a cross-linked structure. Preferably, the UHMWPE is substantially not oxidized and is substantially oxidation resistant. In certain embodiments, the UHMWPE has three melting peaks. In certain embodiments, the UHMWPE has two melting peaks. In certain embodiments, the UHMWPE has one melting peak.

Preferably, the UHMWPE has two melting peaks. Depending upon the particular processing used to make the UHMWPE, certain impurities may be present in the UHMWPE of this invention, including, e.g., calcium stearate, mold release agents, extenders, anti-oxidants and/or other conventional additives to polyethylene polymers.

The invention also provides a method for making cross-linked UHMWPE having substantially no detectable free radicals. Preferably, this UHMWPE is for use as a load bearing article with high wear resistance. Conventional UHMWPE having polymeric chains is provided. The conventional UHMWPE can be in the form of, e.g., a bar stock, a shaped bar stock, e.g., a puck, a coating, or a fabricated article, e.g., a cup or tray shaped article for use in a medical prosthesis. By conventional UHMWPE is meant commercially available high density (linear) polyethylene of molecular weights greater than about 500,000. Preferably, the UHMWPE starting material has an average molecular weight of greater than about 2 million. By initial average molecular weight is meant the average molecular weight of the UHMWPE starting material, prior to any irradiation. The UHMWPE is irradiated so as to cross-link the polymeric chains. The irradiation can be done in an inert or non-inert environment. Preferably, the irradiation is done in a non-inert environment, e.g., air. The irradiated UHMWPE is heated above the melting temperature of the UHMWPE so that there are substantially no detectable free radicals in the UHMWPE. The heated UHMWPE is then cooled to room temperature. Preferably, the cooling step is at a rate greater than about 0.1°C/minute. Optionally, the cooled UHMWPE can be machined. For example, if any oxidation of the UHMWPE occurred during the irradiating step, it can be machined away if desired, by any method known to those skilled in the art. And optionally, the cooled UHMWPE, or the machined UHMWPE, can be sterilized by any method known to those skilled in the art.

One preferred embodiment of this method is called CIR-SM, i.e., cold irradiation and subsequent melting. In this embodiment, the UHMWPE that is provided is at room temperature or below room temperature. Preferably, it is about 20°C. Irradiation of the UHMWPE can be with, e.g., gamma irradiation

or electron irradiation. In general, gamma irradiation gives a high penetration depth but takes a longer time, resulting in the possibility of more in-depth oxidation. In general, electron irradiation gives more limited penetration depths but takes a shorter time, and the possibility of extensive oxidation is reduced. The irradiation is done so as to cross-link the polymeric chains. The irradiation dose can be varied to control the degree of cross-linking and crystallinity in the final UHMWPE product. Preferably, the total absorbed dose of the irradiation is about 0.5 to about 1,000 Mrad, more preferably about 1 to about 100 Mrad, more preferably yet about 4 to about 30 Mrad, more preferably yet about 20 Mrad, and most preferably about 15 Mrad. Preferably, a dose rate is used that does not generate enough heat to melt the UHMWPE. If gamma irradiation is used, the preferred dose rate is about 0.05 to about 0.2 Mrad/minute. If electron irradiation is used, preferably the dose rate is about 0.05 to about 3,000 Mrad/minute, more preferably about 0.05 to about 5 Mrad/minute, and most preferably about 0.05 to about 0.2 Mrad/minute. The dose rate in electron irradiation is determined by the following parameters: (i) the power of the accelerator in kW, (ii) the conveyor speed, (iii) the distance between the surface of the irradiated specimen and the scan horn, and (iv) the scan width. The dose rate at an e-beam facility is often measured in Mrads per pass under the rastering e-beam. The dose rates indicated herein as Mrad/minute can be converted to Mrad/pass by using the following equation:

$$D_{\text{Mrad/min}} = D_{\text{Mrad/pass}} \times v_c \div l$$

where $D_{\text{Mrad/min}}$ is the dose rate in Mrad/min, $D_{\text{Mrad/pass}}$ is the dose rate in Mrad/pass, v_c is the conveyor speed and l is the length of the specimen that travels through the e-beam raster area. When electron irradiation is used, the energy of the electrons can be varied to change the depth of penetration of the electrons. Preferably, the energy of the electrons is about 0.5 MeV to about 12 MeV, more preferably about 5 MeV to about 12 MeV. Such manipulability is particularly useful when the irradiated object is an article of varying thickness or depth,

e.g., an articular cup for a medical prosthesis.

The irradiated UHMWPE is heated above the melting temperature of the UHMWPE so that there are no detectable free radicals in the UHMWPE. The heating provides the molecules with
5 sufficient mobility so as to eliminate the constraints derived from the crystals of the UHMWPE, thereby allowing essentially all of the residual free radicals to recombine. Preferably, the UHMWPE is heated to a temperature of about 137°C to about 300°C, more preferably about 140°C to about 300°C, more preferably yet
10 about 140°C to about 190°C, more preferably yet about 145°C to about 300°C, more preferably yet about 145°C to about 190°C, more preferably yet about 146°C to about 190°C, and most preferably about 150°C. Preferably, the temperature in the heating step is maintained for about 0.5 minutes to about 24
15 hours, more preferably about 1 hour to about 3 hours, and most preferably about 2 hours. The heating can be carried out, e.g., in air, in an inert gas, e.g., nitrogen, argon or helium, in a sensitizing atmosphere, e.g., acetylene, or in a vacuum. It is preferred that for the longer heating times, that the heating be
20 carried out in an inert gas or under vacuum.

Another preferred embodiment of this method is called WIR-SM, i.e., warm irradiation and subsequent melting. In this embodiment, the UHMWPE that is provided is pre-heated to a temperature below the melting temperature of the UHMWPE. The
25 pre-heating can be done in an inert or non-inert environment. It is preferred that this pre-heating is done in air. Preferably, the UHMWPE is pre-heated to a temperature of about 20°C to about 135°C, more preferably to a temperature greater than about 20°C to about 135°C, and most preferably to a
30 temperature of about 50°C. The other parameters are as described above for the CIR-SM embodiment, except that the dose rate for the irradiating step using electron irradiation is preferably about 0.05 to about 10 Mrad/minute, and more preferably is about 4 to about 5 Mrad/minute; and the dose rate
35 for the irradiating step using gamma irradiation is preferably about 0.05 to about 0.2 Mrad/minute, and more preferably is about 0.2 Mrad/minute.

Another preferred embodiment of this method is called WIR-AM, i.e., warm irradiation and adiabatic melting. In this

embodiment, the UHMWPE that is provided is pre-heated to a temperature below the melting temperature of the UHMWPE. The pre-heating can be done in an inert or non-inert environment. It is preferred that this pre-heating is done in air. The pre-heating can be done, e.g., in an oven. It is preferred that the pre-heating is to a temperature between about 100°C to below the melting temperature of the UHMWPE. Preferably, the UHMWPE is pre-heated to a temperature of about 100°C to about 135°C, more preferably the temperature is about 130°C, and most preferably is about 120°C. Preferably, the UHMWPE is in an insulating material so as to reduce heat loss from the UHMWPE during processing. The heat is meant to include, e.g., the pre-heat delivered before irradiation and the heat generated during irradiation. By insulating material is meant any type of material which has insulating properties, e.g., a fiberglass pouch.

The pre-heated UHMWPE is then irradiated to a high enough total dose and at a fast enough dose rate so as to generate enough heat in the polymer to melt substantially all the crystals in the material and thus ensure elimination of substantially all detectable free radicals generated by, e.g., the irradiating step. It is preferred that the irradiating step use electron irradiation so as to generate such adiabatic heating. By adiabatic heating is meant no loss of heat to the surroundings during irradiation. Adiabatic heating results in adiabatic melting if the temperature is above the melting point. Adiabatic melting is meant to include complete or partial melting. The minimum total dose is determined by the amount of heat necessary to heat the polymer from its initial temperature (i.e., the pre-heated temperature discussed above) to its melting temperature, and the heat necessary to melt all the crystals, and the heat necessary to heat the polymer to a pre-determined temperature above its melting point. The following equation describes how the amount of total dose is calculated:

$$\text{Total Dose} = c_{p_s} (T_m - T_i) + \Delta H_m + c_{p_s} (T_f - T_m)$$

where c_{p_s} (= 2 J/g/°C) and c_{p_m} (= 3 J/g/°C) are heat

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capacities of UHMWPE in the solid state and melt state, respectively, ΔH_m (= 146 J/g) is the heat of melting of the unirradiated Hoescht Celanese GUR 415 bar stock, T_i is the initial temperature, and T_f is the final temperature. The final
5 temperature should be above the melting temperature of the UHMWPE.

Preferably, the final temperature of the UHMWPE is about 140°C to about 200°C, more preferably it is about 145°C to about 190°C, more preferably yet it is about 146°C to about 190°C, and
10 most preferably it is about 150°C. At above 160°C, the polymer starts to form bubbles and cracks. Preferably, the dose rate of the electron irradiation is about 2 to about 3,000 Mrad/minute, more preferably yet is about 2 to about 30 Mrad/minute, more preferably yet is about 7 to about 25 Mrad/minute, more
15 preferably yet is about 20 Mrad/minute, and most preferably is about 7 Mrad/minute. Preferably, the total absorbed dose is about 1 to about 100 Mrad. Using the above equation, the absorbed dose for an initial temperature of 130°C and a final temperature of 150°C is calculated to be about 22 Mrad.

20 In this embodiment, the heating step of the method results from the adiabatic heating described above.

In certain embodiments, the adiabatic heating completely melts the UHMWPE. In certain embodiments, the adiabatic heating only partially melts the UHMWPE. Preferably, additional heating
25 of the irradiated UHMWPE is done subsequent to the irradiation induced adiabatic heating so that the final temperature of the UHMWPE after the additional heating is above the melting temperature of the UHMWPE, so as to ensure complete melting of the UHMWPE. Preferably, the temperature of the UHMWPE from the
30 additional heating is about 140°C to about 200°C, more preferably is about 145°C to about 190°C, more preferably yet is about 146°C to about 190°C, and most preferably is about 150°C.

Yet another embodiment of this invention is called CIR-AM, i.e., cold irradiation and adiabatic heating. In this
35 embodiment, UHMWPE at room temperature or below room temperature is melted by adiabatic heating, with or without subsequent additional heating, as described above.

This invention also includes the product made in accordance with the above described method.

Also provided in this invention is a method of making a medical prosthesis from UHMWPE having substantially no detectable free radicals, the prosthesis resulting in the reduced production of particles from the prosthesis during wear of the prosthesis. Radiation treated UHMWPE having no detectable free radicals is provided. A medical prosthesis is formed from this UHMWPE so as to reduce production of particles from the prosthesis during wear of the prosthesis, the UHMWPE forming a load bearing surface of the prosthesis. Formation of the prosthesis can be accomplished by standard procedures known to those skilled in the art, e.g., machining.

Also provided in this invention is a method of treating a body in need of a medical prosthesis. A shaped prosthesis formed of radiation treated UHMWPE having substantially no detectable free radicals is provided. This prosthesis is applied to the body in need of the prosthesis. The prosthesis reduces production of fine particles from the prosthesis during wear of the prosthesis. In preferred embodiments, the ultra high molecular weight polyethylene forms a load bearing surface of the prosthesis.

In yet another embodiment of this invention, a medical prosthesis for use within the body which is formed of ultra high molecular weight polyethylene (UHMWPE) which has a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus, so as to reduce production of fine particles from the prosthesis during wear of the prosthesis, is provided.

The UHMWPE of this embodiment has a polymeric structure with less than about 50% crystallinity, preferably less than about 40% crystallinity. By crystallinity is meant the fraction of the polymer that is crystalline. The crystallinity is calculated by knowing the weight of the sample (w , in g), the heat absorbed by the sample in melting (E , in cal) and the calculated heat of melting of polyethylene in the 100% crystalline state ($\Delta H^\circ = 69.2$ cal/g), and using the following equation:

$$\% \text{ crystallinity} = \frac{E}{w \cdot \Delta H^\circ}$$

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The UHMWPE of this embodiment has a polymeric structure with less than about 290Å lamellar thickness, preferably less than about 200Å lamellar thickness, and most preferably less than about 100Å lamellar thickness. By lamellar thickness (1) is meant the calculated thickness of assumed lamellar structures in the polymer using the following expression:

$$l = \frac{2 \cdot \sigma_e \cdot T_m^\circ}{\Delta H^\circ \cdot (T_m^\circ - T_m) \cdot \rho}$$

where, σ_e is the end free surface energy of polyethylene (2.22×10^{-6} cal/cm²), ΔH° is the calculated heat of melting of polyethylene in the 100% crystalline state (69.2 cal/g), ρ is the density of the crystalline regions (1.005 g/cm³), T_m° is the melting point of a perfect polyethylene crystal (418.15K) and T_m is the experimentally determined melting point of the sample.

The UHMWPE of this embodiment has less than about 940 MPa tensile elastic modulus, preferably less than about 600 MPa tensile elastic modulus, more preferably less than about 400 MPa tensile elastic modulus, and most preferably less than about 200 MPa tensile elastic modulus. By tensile elastic modulus is meant the ratio of the nominal stress to corresponding strain for strains less than 0.5% as determined using the standard test ASTM 638 M III.

Preferably, the UHMWPE of this embodiment has a polymeric structure with about 40% crystallinity, about 100Å lamellar thickness and about 200 MPa tensile elastic modulus.

The UHMWPE of this embodiment has no trapped free radicals, e.g., unsaturated trans-vinylene free radicals. It is preferred that the UHMWPE of this embodiment have a hardness less than about 65 on the Shore D scale, more preferably a hardness less than about 55 on the Shore D scale, most preferably a hardness less than about 50 on the Shore D scale. By hardness is meant the instantaneous indentation hardness measured on the Shore D scale using a durometer described in ASTM D2240. It is preferred that the UHMWPE of this embodiment be substantially not oxidized. The polymeric structure has extensive cross-linking such that a substantial portion of the polymeric structure does not dissolve in Decalin. By substantial portion

is meant at least 50% of the polymer sample's dry weight. By not dissolve in Decalin is meant does not dissolve in Decalin at 150°C over a period of 24 hours. Preferably, the UHMWPE of this embodiment has a high density of entanglement so as to cause the formation of imperfect crystals and reduce crystallinity. By the density of entanglement is meant the number of points of entanglement of polymer chains in a unit volume; a higher density of entanglement being indicated by the polymer sample's inability to crystallize to the same extent as conventional UHMWPE, thus leading to a lesser degree of crystallinity.

The invention also includes other fabricated articles made from the UHMWPE of this embodiment having a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus. Such articles include shaped articles and unshaped articles, including, e.g., machined objects, e.g., cups, gears, nuts, sled runners, bolts, fasteners, cables, pipes and the like, and bar stock, films, cylindrical bars, sheeting, panels, and fibers. Shaped articles can be made, e.g., by machining. The fabricated articles are particularly suitable for load bearing applications, e.g., as a load bearing surface, and as metal replacement articles. Thin films or sheets of UHMWPE, which have been melt-irradiated can also be attached, e.g., with glue, onto supporting surfaces, and thus used as a transparent, wear resistant load bearing surface.

The invention also includes an embodiment in which UHMWPE has a unique polymeric structure characterized by less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus. Depending upon the particular processing used to make the UHMWPE, certain impurities may be present in the UHMWPE of this invention, including, e.g., calcium stearate, mold release agents, extenders, anti-oxidants and/or other conventional additives to polyethylene polymers. In certain embodiments, the UHMWPE has high transmissivity of light, preferably a transmission greater than about 10% of light at 517 nm through a 1 mm thick sample, more preferably a transmission greater than about 30% of light at 517 nm through a 1 mm thick sample, and most preferably a transmission greater than about 40% of light at 517 nm through a

1 mm thick sample. Such UHMWPE is particularly useful for thin films or sheets which can be attached onto supporting surfaces of various articles, the film or sheet being transparent and wear resistant.

5 In another embodiment of this invention, a method for making crosslinked UHMWPE is provided. This method is called melt irradiation (MIR). Conventional UHMWPE is provided. Preferably, the UHMWPE is surrounded with an inert material that is substantially free of oxygen. The UHMWPE is heated above the
10 melting temperature of the UHMWPE so as to completely melt all crystalline structure. The heated UHMWPE is irradiated, and the irradiated UHMWPE is cooled to about 25°C.

Preferably, the UHMWPE made from this embodiment has a polymeric structure with less than about 50% crystallinity, less
15 than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus. Conventional UHMWPE, e.g., a bar stock, a shaped bar stock, a coating, or a fabricated article is provided. By conventional UHMWPE is meant commercially available high density (linear) polyethylene of molecular
20 weights greater than about 500,000. Preferably, the UHMWPE starting material has an average molecular weight of greater than about 2 million. By initial average molecular weight is meant the average molecular weight of the UHMWPE starting material, prior to any irradiation. It is preferred that this
25 UHMWPE is surrounded with an inert material that is substantially free of oxygen, e.g., nitrogen, argon or helium. In certain embodiments, a non-inert environment can be used. The UHMWPE is heated above its melting temperature for a time sufficient to allow all the crystals to melt. Preferably, the
30 temperature is about 145°C to about 230°C, and more preferably, is about 175° to about 200°C. Preferably, the heating is maintained so to keep the polymer at the preferred temperature for about 5 minutes to about 3 hours, and more preferably for about 30 minutes to about 2 hours. The UHMWPE is then
35 irradiated with gamma irradiation or electron irradiation. In general, gamma irradiation gives a high penetration depth but takes a longer time, resulting in the possibility of some oxidation. In general, electron irradiation gives more limited penetration depths but takes a shorter time, and hence the

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possibility of oxidation is reduced. The irradiation dose can be varied to control the degree of crosslinking and crystallinity in the final UHMWPE product. Preferably, a dose of greater than about 1 Mrad is used, more preferably a dose of greater than about 20 Mrad is used. When electron irradiation is used, the energy of the electrons can be varied to change the depth of penetration of the electrons, thereby controlling the degree of crosslinking and crystallinity in the final UHMWPE product. Preferably, the energy is about 0.5 MeV to about 12 MeV, more preferably about 1 MeV to about 10 MeV, and most preferably about 10 MeV. Such manipulability is particularly useful when the irradiated object is an article of varying thickness or depth, e.g., an articular cup for a prosthesis. The irradiated UHMWPE is then cooled to about 25°C. Preferably, the cooling rate is equal to or greater than about 0.5°C/min, more preferably equal to or greater than about 20°C/min. In certain embodiments, the cooled UHMWPE can be machined. In preferred embodiments, the cooled irradiated UHMWPE has substantially no detectable free radicals. Examples 1, 3 and 6 describe certain preferred embodiments of the method. Examples 2, 4 and 5, and FIGS. 4 through 7, illustrate certain properties of the melt-irradiated UHMWPE obtained from these preferred embodiments, as compared to conventional UHMWPE.

This invention also includes the product made in accordance with the above described method.

In an embodiment of MIR, highly entangled and crosslinked UHMWPE is made. Conventional UHMWPE is provided. Preferably, the UHMWPE is surrounded with an inert material that is substantially free of oxygen. The UHMWPE is heated above the melting temperature of the UHMWPE for a time sufficient to enable the formation of entangled polymer chains in the UHMWPE. The heated UHMWPE is irradiated so as to trap the polymer chains in the entangled state. The irradiated UHMWPE is cooled to about 25°C.

This invention also includes the product made in accordance with the above described method.

Also provided in this invention is a method of making a prosthesis from UHMWPE so as to reduce production of fine particles from the prosthesis during wear of the prosthesis.

UHMWPE having a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus is provided. A prosthesis is formed from this UHMWPE, the UHMWPE forming a load bearing surface of the prosthesis. Formation of the prosthesis can be accomplished by standard procedures known to those skilled in the art, e.g., machining.

Also provided in this invention is a method of treating a body in need of a prosthesis. A shaped prosthesis formed of ultra high molecular weight polyethylene having a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus, is provided. This prosthesis is applied to the body in need of the prosthesis. The prosthesis reduces production of fine particles from the prosthesis during wear of the prosthesis. In preferred embodiments, the ultra high molecular weight polyethylene forms a load bearing surface of the prosthesis.

The products and processes of this invention also apply to other polymeric materials such as high-density-polyethylene, low-density-polyethylene, linear-low-density-polyethylene and polypropylene.

The following non-limiting examples further illustrate the present invention.

EXAMPLES

Example 1: Method of Making Melt-Irradiated UHMWPE (MIR)

This example illustrates electron irradiation of melted UHMWPE.

A cuboidal specimen (puck) of size 10 mm x 12 mm x 60 mm, prepared from conventional ram extruded UHMWPE bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was placed in a chamber. The atmosphere within the chamber consisted of low oxygen nitrogen gas (<0.5 ppm oxygen gas) (obtained from AIRCO, Murray Hill, NJ). The pressure in the chamber was approximately 1 atm. The temperature of the sample and the irradiation chamber was controlled using a heater, a variac and a thermocouple readout (manual) or temperature controller (automatic). The chamber was

heated with a 270 W heating mantle. The chamber was heated (controlled by the variac) at a rate such that the steady state temperature of the sample was about 175°C. The sample was held at the steady state temperature for 30 minutes before starting the irradiation.

Irradiation was done using a van de Graaff generator with electrons of energy 2.5 MeV and a dose rate of 1.67 MRad/min. The sample was given a dose of 20 MRad with the electron beam hitting the sample on the 60 mm x 12 mm surface. The heater was switched off after irradiation, and the sample was allowed to cool within the chamber under inert atmosphere, nitrogen gas, to 25°C at approximately 0.5°C/minute. As a control, similar specimens were prepared using unheated and unirradiated bar stock of conventional UHMWPE.

15

Example 2: Comparison of Properties of GUR 415 UHMWPE Bar Stock and Melt-Irradiated (MIR) GUR 415 UHMWPE Bar Stock (20 MRad)

This example illustrates various properties of the irradiated and unirradiated samples of UHMWPE bar stock (GUR 415) obtained from Example 1. The tested samples were as follows: the test sample was bar stock which was molten and then irradiated while molten; control was bar stock (no heating/melting, no irradiation).

25

(A) Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC7 was used with an ice-water heat sink and a heating and cooling rate of 10°C/minute with a continuous nitrogen purge. The crystallinity of the samples obtained from Example 1 was calculated from the weight of the sample and the heat of melting of polyethylene crystals (69.2 cal/g). The temperature corresponding to the peak of the endotherm was taken as the melting point. The lamellar thickness was calculated by assuming a lamellar crystalline morphology, and knowing ΔH° the heat of melting of 100% crystalline polyethylene (69.2 cal/g), the melting point of a perfect crystal (418.15 K), the density of the crystalline regions (1.005 g/cm³) and the end free surface energy of polyethylene (2.22 x 10⁻⁶ cal/cm²). The results are shown in Table 1 and FIG. 4.

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Table 1: DSC (10°C/min)

5	<u>Property</u>	GUR 415	GUR 415
		(unirradiated)	(melt-irradiated)
		<u>0 MRad</u>	<u>20 MRad</u>
	Crystallinity (%)	50.2	37.8
	Melting Point (C)	135.8	125.5
	Lamellar thickness (Å)	290	137

10

The results indicate that the melt-irradiated sample had a more entangled and less crystalline polymeric structure than the unirradiated sample, as evidenced by lower crystallinity, lower lamellar thickness and lower melting point.

15

(B) Swell Ratio

The samples were cut into cubes of size 2 mm x 2 mm x 2 mm and kept submerged in Decalin at 150°C for a period of 24 hours. An antioxidant (1% N-phenyl-2-naphthylamine) was added to the Decalin to prevent degradation of the sample. The swell ratio and percent extract were calculated by measuring the weight of the sample before the experiment, after swelling for 24 hours and after vacuum drying the swollen sample. The results are shown in Table 2.

25

Table 2: Swelling in Decalin with Antioxidant for 24 hours at 150°C

30	<u>Property</u>	GUR 415	GUR 415
		(unirradiated)	(melt-irradiated)
		<u>0 MRad</u>	<u>20 MRad</u>
	Swell Ratio	dissolves	2.5
	Extract (%)	approx. 100%	0.0

35

The results indicate that the melt-irradiated UHMWPE sample was highly crosslinked, and hence did not allow dissolution of polymer chains into the hot solvent even after 24 hours, while the unirradiated sample dissolved completely in the hot solvent in the same period.

40

(C) Tensile Elastic Modulus

ASTM 638 M III of the samples was followed. The displacement rate was 1 mm/minute. The experiment was performed on a MTS machine. The results are shown in Table 3.

45

Table 3: Elastic Test (ASTM 638 M III, 1 mm/min.

Property	GUR 415 (unirradiated)	GUR 415 (melt-irradiated)
	<u>0 MRad</u>	<u>20 MRad</u>
Tensile Elastic modulus (MPa)	940.7	200.8
Yield stress	22.7	14.4
Strain at break (%)	953.8	547.2
Engineering UTS (MPa)	46.4	15.4

The results indicate that the melt-irradiated UHMWPE sample had a significantly lower tensile elastic modulus than the unirradiated control. The lower strain at break of the melt-irradiated UHMWPE sample is yet further evidence for the crosslinking of chains in that sample.

(D) Hardness

The hardness of the samples was measured using a durometer on the shore D scale. The hardness was recorded for instantaneous indentation. The results are shown in Table 4.

Table 4: Hardness (Shore D)

Property	GUR 415 (unirradiated)	GUR 415 (melt-irradiated)
	<u>0 MRad</u>	<u>20 MRad</u>
Hardness (D Scale)	65.5	54.5

The results indicate that the melt-irradiated UHMWPE was softer than the unirradiated control.

(E) Light Transmissivity (transparency)

Transparency of the samples was measured as follows: Light transmission was studied for a light of wave length 517 nm passing through a sample of approximately 1 mm in thickness placed between two glass slides. The samples were prepared by polishing the surfaces against 600 grit paper. Silicone oil was spread on the surfaces of the sample and then the sample was placed in between two slides. The silicone oil was used in order to reduce diffuse light scattering due to the surface roughness of the polymer sample. The reference used for this purpose was two similar glass slides separated by a thin film of silicone oil. The transmissivity was measured using a Perkin

Elmer Lambda 3B uv-vis spectrophotometer. The absorption coefficient and transmissivity of a sample exactly 1 mm thick were calculated using the Lambert-Beer law. The results are shown in Table 5.

5 Table 5: Transmissivity of Light at 517 nm

<u>Property</u>	GUR 415 (unirradiated) <u>0 MRad</u>	GUR 415 (melt-irradiated) <u>20 MRad</u>
10 Transmission (%) (1 mm sample)	8.59	39.9
15 Absorption coefficient (cm ⁻¹)	24.54	9.18

The results indicate that the melt-irradiated UHMWPE sample transmitted much more light through it than the control, and hence is much more transparent than the control.

(F) Environmental Scanning Electron Microscopy (ESEM)

ESEM (ElectroScan, Model 3) was performed on the samples at 10 kV (low voltage to reduce radiation damage to the sample) with an extremely thin gold coating (approximately 20Å to enhance picture quality). By studying the surface of the polymer under the ESEM with and without the gold coating, it was verified that the thin gold coating did not produce any artifacts.

30 The samples were etched using a permanganate etch with a 1:1 sulfuric acid to orthophosphoric acid ratio and a 0.7% (w/v) concentration of potassium permanganate before being viewed under the ESEM.

FIG. 4 shows an ESEM (magnification of 10,000 x) of an etched surface of conventional UHMWPE (GUR 415; unheated; unirradiated). FIG. 5 shows an ESEM (magnification of 10,500 x) of an etched surface of melt-irradiated UHMWPE (GUR 415; melted; 20 MRad). The ESEMs indicated a reduction in size of the crystallites and the occurrence of imperfect crystallization in the melt-irradiated UHMWPE as compared to the conventional UHMWPE.

(G) Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR of the samples was performed using a micro sampler on the samples rinsed with hexane to remove surface impurities.

The peaks observed around 1740 to 1700 cm^{-1} are bands associated with oxygen containing groups. Hence, the ratio of the area under the carbonyl peak at 1740 cm^{-1} to the area under the methylene peak at 1460 cm^{-1} is a measure of the degree of oxidation.

The FTIR spectra indicate that the melt-irradiated UHMWPE sample showed more oxidation than the conventional unirradiated UHMWPE control, but a lot less oxidation than an UHMWPE sample irradiated in air at room temperature and given the same irradiation dose as the melt-irradiated sample.

(H) Electron Paramagnetic Resonance (EPR)

EPR was performed at room temperature on the samples which were placed in a nitrogen atmosphere in an air tight quartz tube. The instrument used was the Bruker ESP 300 EPR spectrometer and the tubes used were Taperlok EPR sample tubes obtained from Wilmad Glass Company, Buena, NJ.

The unirradiated samples do not have any free radicals in them since irradiation is the process which creates free radicals in the polymer. On irradiation, free radicals are created which can last for several years under the appropriate conditions.

The EPR results indicate that the melt-irradiated sample did not show any free radicals when studied using an EPR immediately after irradiation, whereas the sample which was irradiated at room temperature under nitrogen atmosphere showed trans-vinylene free radicals even after 266 days of storage at room temperature. The absence of free radicals in the melt-irradiated UHMWPE sample means that any further oxidative degradation was not possible.

(I) Wear

The wear resistance of the samples was measured using a bi-axial pin-on-disk wear tester. The wear test involved the rubbing action of UHMWPE pins (diameter = 9 mm; height = 13 mm) against a Co-Cr alloy disk. These tests were carried out to a total of 2 million cycles. The unirradiated pin displayed a wear rate of 8 mg/million-cycles while the irradiated pin had a wear rate of 0.5 mg/million cycles. The results indicate that the melt-irradiated UHMWPE has far superior wear resistance than the unirradiated control.

Example 3: Method of Making Melt-Irradiated (MIR) UHMWPE Conventional Articular Cups

This example illustrates electron irradiation of a melted
5 UHMWPE conventional articular cup.

A conventional articular cup (high conformity unsterilized UHMWPE cup made by Zimmer, Inc., Warsaw, IN) of internal diameter 26 mm and made of GUR 415 ram extruded bar stock, was irradiated under controlled atmosphere and temperature condi-
10 tions in an air-tight chamber with a titanium cup holder at the base and a thin stainless steel foil (0.001 inches thick) at the top. The atmosphere within this chamber consisted of low oxygen nitrogen gas (< 0.5 ppm oxygen gas) (obtained from AIRCO, Murray Hill, NH). The pressure in the chamber was approximately 1 atm.
15 The chamber was heated using a 270 W heating mantle at the base of the chamber which was controlled using a temperature controller and a variac. The chamber was heated such that the temperature at the top surface of the cup rose at approximately 1.5° to 2°C/min, finally asymptotically reaching a steady state temperature of approximately 175°C. Due to the thickness of the sample
20 cup and the particular design of the equipment used, the steady state temperature of the cup varied between 200°C at the base to 175°C at the top. The cup was held at these temperatures for a period of 30 minutes before starting the irradiation.

Irradiation was done using a van de Graaff generator with
25 electrons of energy 2.5 MeV and a dose rate of 1.67 MRad/min. The beam entered the chamber through the thin foil at top and hit the concave surface of the cup. The dose received by the cup was such that a maximum dose of 20 MRad was received
30 approximately 5 mm below the surface of the cup being hit by the electrons. After irradiation, the heating was stopped and the cup was allowed to cool to room temperature (approximately 25°C) while still in the chamber with nitrogen gas. The rate of cooling was approximately 0.5°C/min. The sample was removed from
35 the chamber after the chamber and the sample had reached room temperature.

The above irradiated cup which increases in volume (due to the decrease in density accompanying the reduction of crystallinity following melt-irradiation) can be remachined to
40 the appropriate dimensions.

Example 4: Swell Ratio and Percent Extract at Different Depths for Melt-Irradiated (MIR) UHMWPE Articular Cups

5 This example illustrates the swell ratio and percent extract at different depths of the melt-irradiated articular cup obtained from Example 3. Samples of size 2 mm x 2 mm x 2 mm were cut from the cup at various depths along the axis of the cup. These samples were then kept submerged in Decalin at 150°C
 10 for a period of 24 hours. An antioxidant (1% N-phenyl-2-naphthylamine) was added to the Decalin to prevent degradation of the sample. The swell ratio and percent extract were calculated by measuring the weight of the sample before the experiment, after swelling for 24 hours, and after vacuum drying
 15 the swollen sample. The results are shown in Table 6.

Table 6: The Swell Ratio and Percent Extract at Different Depths on the Melt-Irradiated UHMWPE Articular Cup

20	<u>Depth (mm)</u>	<u>Swell Ratio (Decalin, 150 °C, 1 day)</u>	<u>% Extract</u>
	0-2	2.43	0.0
	2-4	2.52	0.0
25	4-6	2.51	0.0
	6-8	2.64	0.0
	8-10	2.49	0.0
	10-12	3.68	0.0
	> 12	6.19	35.8
30	Unirradiated	Dissolves	Approx. 100%

The results indicate that the UHMWPE in the cup had been crosslinked to a depth of 12 mm due to the melt-irradiation
 35 process to such an extent that no polymer chains dissolved out in hot Decalin over 24 hours.

Example 5: Crystallinity and Melting Point at Different Depths for the Melt-Irradiated (MIR) UHMWPE Articular Cups

40 This example illustrates the crystallinity and melting point at different depths of the melt-irradiated cup obtained from Example 3.

45 Samples were taken from the cup at various depths along the axis of the cup. The crystallinity is the fraction of the polymer that is crystalline. The crystallinity was calculated

by knowing the weight of the sample (w, in g), the heat absorbed by the sample in melting (E, in cal which was measured experimentally using a Differential Scanning Calorimeter at 10°C/min) and the heat of melting of polyethylene in the 100% crystalline state ($\Delta H^\circ = 69.2$ cal/g), using the following equation:

$$\% \text{ crystallinity} = \frac{E}{w \cdot \Delta H^\circ}$$

The melting point is the temperature corresponding to the peak in the DSC endotherm. The results are shown in FIG. 7.

The results indicate that the crystallinity and the melting point of the melt-irradiated UHMWPE in the articular cups obtained from Example 3 were much lower than the corresponding values of the conventional UHMWPE, even to a depth of 1 cm (the thickness of the cup being 1.2 cms).

Example 6: Second Method of Making Melt-Irradiated (MIR) UHMWPE Articular Cups

This example illustrates a method for making articular cups with melt-irradiated UHMWPE.

Conventional ram extruded UHMWPE bar stock (GUR 415 bar stock obtained from West Lake Plastics, Lenni, PA) was machined to the shape of a cylinder, of height 4 cm and diameter 5.2 cm. One circular face of the cylinder was machined to include an exact hemispherical hole, of diameter 2.6 cm, such that the axis of the hole and the cylinder coincided. This specimen was enclosed in an air-tight chamber with a thin stainless steel foil (0.001 inches thick) at the top. The cylindrical specimen was placed such that the hemispherical hole faced the foil. The chamber was then flushed and filled with an atmosphere of low oxygen nitrogen gas (<0.5 ppm oxygen gas) obtained from AIRCO, Murray Hill, NJ). Following this flushing and filling, a slow continuous flow of nitrogen was maintained while keeping the pressure in the chamber at approximately 1 atm. The chamber was heated using a 270 W heating mantle at the base of the chamber which was controlled using a temperature controller and a variac. The chamber was heated such that the temperature at the top surface of the cylindrical specimen rose at approximately 1.5°C to 2°C/min, finally asymptotically reaching a steady state

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temperature of approximately 175°C. The specimen was then held at this temperature for a period of 30 minutes before starting irradiation.

Irradiation was done using a van de Graaff generator with
5 electrons of energy 2.5 MeV and a dose rate of 1.67 MRad/min. The beam entered the chamber through the thin foil at top and hit the surface with the hemispherical hole. The dose received by the specimen was such that a maximum dose of 20 MRad was received approximately 5 mm below the surface of the polymer
10 being hit by the electrons. After irradiation, the heating was stopped and the specimen was allowed to cool to room temperature (approximately 25°C) while still in the chamber with nitrogen gas. The rate of cooling was approximately 0.5°C/min. The sample was removed from the chamber after the chamber and the
15 sample had reached room temperature.

This cylindrical specimen was then machined into an articular cup with the dimensions of a high conformity UHMWPE articular cup of internal diameter 26 mm manufactured by Zimmer, Inc., Warsaw, IN, such that the concave surface of the
20 hemispherical hole was remachined into the articulating surface. This method allows for the possibility of relatively large changes in dimensions during melt irradiation.

Example 7: Electron Irradiation of UHMWPE Pucks

25 This example illustrates that electron irradiation of UHMWPE pucks gives a non-uniform absorbed dose profile.

Conventional UHMWPE ram extruded bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was used. The GUR 415 resin used for the bar stock
30 had a molecular weight of 5,000,000 g/mol and contained 500 ppm of calcium stearate. The bar stock was cut into "hockey puck" shaped cylinders (height 4 cm, diameter 8.5 cm).

The pucks were irradiated at room temperature with an electron-beam incident to one of the circular bases of the pucks
35 with a linear electron accelerator operated at 10 MeV and 1 kW (AECL, Pinawa, Manitoba, Canada), with a scan width of 30 cm and a conveyor speed of 0.08 cm/sec. Due to a cascade effect, electron beam irradiation results in a non-uniform absorbed dose profile. Table 7 illustrates the calculated absorbed dose

values at various depths in a specimen of polyethylene irradiated with 10 MeV electrons. The absorbed doses were the values measured at the top surface (surface of e-beam incidence).

5 Table 7: The variation of absorbed dose as a function of depth in polyethylene

	<u>Depth (mm)</u>	<u>Absorbed Dose (Mrad)</u>
	0	20
10	0.5	22
	1.0	23
	1.5	24
	2.0	25
	2.5	27
15	3.0	26
	3.5	23
	4.0	20
	4.5	8
	5.0	3
20	5.5	1
	6.0	0

25 Example 8: Method of Making UHMWPE Using Cold Irradiation and Subsequent Melting (CIR-SM)

This example illustrates a method of making UHMWPE that has a cross-linked structure and has substantially no detectable free radicals, by cold irradiating and then melting the UHMWPE.

30 Conventional UHMWPE ram extruded bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was used. The GUR 415 resin used for the bar stock had a molecular weight of 5,000,000 g/mol and contained 500 ppm of calcium stearate. The bar stock was cut into "hockey puck" shaped cylinders (height 4 cm, diameter 8.5 cm).

The pucks were irradiated at room temperature at a dose rate of 2.5 Mrad per pass to 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 30, and 50 Mrad total absorbed dose as measured on the top surface (electron-beam incidence) (AECL, Pinawa, Manitoba, Canada). The pucks were not packaged and the irradiation was carried out in air. Subsequent to irradiation, the pucks were heated to 150°C under vacuum for 2 hours so as to melt the polymer and thereby result in the recombination of free radicals leading to substantially no detectable residual free radicals. The pucks were then cooled to room temperature at a rate of 5°C/min.

The residual free radicals are measured by electron paramagnetic resonance as described in Jahan et al., J. Biomedical Materials Research 25:1005 (1991).

5 Example 9: Method of Making UHMWPE Using Warm Irradiation and Subsequent Melting (WIR-SM)

 This example illustrates a method of making UHMWPE that has a cross-linked structure and has substantially no detectable
10 free radicals, by irradiating UHMWPE that has been heated to below the melting point, and then melting the UHMWPE.

 Conventional UHMWPE ram extruded bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was used. The GUR 415 resin used for the bar stock
15 had a molecular weight of 5,000,000 g/mol and contained 500 ppm of calcium stearate. The bar stock was cut into "hockey puck" shaped cylinders (height 4 cm, diameter 8.5 cm).

 The pucks were heated to 100°C in air in an oven. The heated pucks were then irradiated with an electron beam to a
20 total dose of 20 Mrad at a dose rate of 2.5 Mrad per pass (E-Beam Services, Cranbury, NJ), with a scan width of 30 cm and a conveyor speed of 0.08 cm/sec. Subsequent to irradiation, the pucks were heated to 150°C under vacuum for 2 hours, thereby allowing the free radicals to recombine leading to substantially
25 no detectable residual free radicals. The pucks were then cooled to room temperature at a rate of 5°C/min.

Example 10: Method of Making UHMWPE Using Warm Irradiation and Adiabatic Melting (WIR-AM)

30 This example illustrates a method of making UHMWPE that has a cross-linked structure and has substantially no detectable free radicals, by irradiating UHMWPE that has been heated to below the melting point so as to generate adiabatic melting of
35 the UHMWPE.

 Conventional UHMWPE ram extruded bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was used. The GUR 415 resin used for the bar stock
40 had a molecular weight of 5,000,000 g/mol and contained 500 ppm of calcium stearate. The bar stock was cut into "hockey puck" shaped cylinders (height 4 cm, diameter 8.5 cm).

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Two pucks were packed in a fiberglass pouch (obtained from Fisher Scientific Co., Pittsburgh, PA) to minimize heat loss in subsequent processing steps. First, the wrapped pucks were heated overnight in an air convection oven kept at 120°C. As soon as the pucks were removed from the oven they were placed under an electron-beam incident to one of the circular bases of the pucks from a linear electron accelerator operated at 10 MeV and 1kW (AECL, Pinawa, Manitoba, Canada), and immediately irradiated to a total dose of 21 and 22.5 Mrad, respectively. The dose rate was 2.7 Mrad/min. Therefore, for 21 Mrad, radiation was for 7.8 min., and for 22.5 Mrad, radiation was for 8.3 min. Following the irradiation, the pucks were cooled to room temperature at a rate of 5°C/minute, at which point the fiberglass pouch was removed and the specimens analyzed.

Example 11: Comparison of Properties of GUR 415 UHMWPE Bar Stock Pucks and CIR-SM and WIR-AM-Treated Bar Stock Pucks

This example illustrates various properties of the irradiated and unirradiated samples of UHMWPE bar stock GUR 415 obtained from Examples 8 and 10. The tested samples were as follows: (i) test samples (pucks) from bar stock which was irradiated at room temperature, subsequently heated to about 150°C for complete melting of polyethylene crystals, followed by cooling to room temperature (CIR-SM), (ii) test samples (pucks) from bar stock which was heated to 120°C in a fiberglass pouch so as to minimize heat loss from the pucks, followed by immediate irradiation to generate adiabatic melting of the polyethylene crystals (WIR-AM), and (iii) control bar stock (no heating/melting, no irradiation).

A. Fourier Transform Infra-Red Spectroscopy (FTIR)

Infra-red (IR) spectroscopy of the samples was performed using a BioRad UMA 500 infrared microscope on thin sections of the samples obtained from Examples 8 and 10. The thin sections (50 μm) were prepared with a sledge microtome. The IR spectra were collected at 20 μm , 100 μm , and 3 mm below the irradiated surface of the pucks with an aperture size of 10 x 50 μm^2 . The peaks observed around 1740 to 1700 cm^{-1} are associated with the

oxygen containing groups. Hence, the ratio of the area under the carbonyl peak at 1740 cm^{-1} to the area under the methylene peak at 1460 cm^{-1} , after subtracting the corresponding baselines, was a measure of the degree of oxidation. Tables 8 and 9

5 summarize the degree of oxidation for the specimens described in Examples 8 and 10.

These data show that following the cross-linking procedures there was some oxidation within a thin layer of about $100\mu\text{m}$ thickness. Upon machining this layer away, the final product
10 would have the same oxidation levels as the unirradiated control.

Table 8: Degree of oxidation of specimens from Example 8 (CIR-SM)(with post-irradiation melting in vacuum)

Specimen	Oxidation Degree at various depths (A.U.)		
	20 μm	100 μm	3 mm
Unirradiated Control	0.01	0.01	0.02
Irradiated to 2.5 Mrad	0.04	0.03	0.03
Irradiated to 5 Mrad	0.04	0.03	0.01
Irradiated to 7.5 Mrad	0.05	0.02	0.02
Irradiated to 10 Mrad	0.02	0.03	0.01
25 Irradiated to 12.5 Mrad	0.04	0.03	0.01
Irradiated to 15 Mrad	0.03	0.01	0.02
Irradiated to 17.5 Mrad	0.07	0.05	0.02
Irradiated to 20 Mrad	0.03	0.02	0.01

Table 9: Degree of oxidation of specimens from Example 10 (WIR-AM)

Specimen	Oxidation Degree at (A.U.)		
	20 μm	100 μm	3 mm
Unirradiated Control	0.01	0.01	0.02
Irradiated to 21 Mrad	0.02	0.01	0.03
Irradiated to 22.5 Mrad	0.02	0.02	0.01

B. Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC7 was used with an ice-water heat sink
45 and a heating and cooling rate of $10^\circ\text{C}/\text{minute}$ with a continuous nitrogen purge. The crystallinity of the specimens obtained from Examples 8 and 10 was calculated from the weight of the sample and the heat of melting of polyethylene crystals measured during the first heating cycle. The percent crystallinity is

given by the following equation:

$$\% \text{ crystallinity} = \frac{E}{w \cdot \Delta H^\circ}$$

where E and w are the heat of melting (J or cal) and weight (grams) of the specimen tested, respectively, and ΔH° is the heat of melting of 100% crystalline polyethylene in Joules/gram (291 J/g or 69.2 cal/g). The temperature corresponding to the peak of the endotherm was taken as the melting point. In some cases where there were multiple endotherm peaks, multiple melting points corresponding to these endotherm peaks have been reported. The crystallinities and melting points for the specimens described in Examples 8 and 10 are reported in Tables 10 and 11.

Table 10: DSC at a heating rate of 10°C/min for specimens of Example 8 (CIR-SM)

<u>Specimen</u>	<u>Crystallinity(%)</u>	<u>Melting Point(°C)</u>
Unirradiated Control	59	137
Irradiated to 2.5 Mrad	54	137
Irradiated to 5 Mrad	53	137
Irradiated to 10 Mrad	54	137
Irradiated to 20 Mrad	51	137
Irradiated to 30 Mrad	37	137

Table 11: DSC at a heating rate of 10°C/min for specimens of Example 10 (WIR-AM)

<u>Specimen</u>	<u>Crystallinity(%)</u>	<u>Melting Point(°C)</u>
Unirradiated Control	59	137
Irradiated to 21 Mrad	54	120-135-145
Irradiated to 22.5 Mrad	48	120-135-145

The data shows that the crystallinity does not change significantly up to absorbed doses of 20 Mrad. Therefore, the elastic properties of the cross-linked material should remain substantially unchanged upon cross-linking. On the other hand, one could tailor the elastic properties by changing the crystallinity with higher doses. The data also shows that the WIR-AM material exhibited three melting peaks.

C. Pin-on-Disc Experiments for Wear Rate

The pin-on-disc (POD) experiments were carried out on a bi-axial pin-on-disc tester at a frequency of 2 Hz where polymeric pins were tested by a rubbing action of the pin against a highly polished Co-Cr disc. Prior to preparing cylindrical shaped pins (height 13 mm, diameter 9 mm), one millimeter from the surface of the pucks was machined away in order to remove the outer layer that had been oxidized during irradiation and post- and pre-processing. The pins were then machined from the core of the pucks and tested on the POD such that the surface of e-beam incidence was facing the Co-Cr disc. The wear tests were carried out to a total of 2,000,000 cycles in bovine serum. The pins were weighed at every 500,000 cycle and the average values of weight loss (wear rate) are reported in Tables 12 and 13 for specimens obtained from Examples 8 and 10 respectively.

Table 12: POD wear rates for specimens of Example 8 (CIR-SM)

<u>Specimen</u>	<u>Wear Rate (mg/million cycle)</u>
Unirradiated Control	9.78
Irradiated to 2.5 Mrad	9.07
Irradiated to 5 Mrad	4.80
Irradiated to 7.5 Mrad	2.53
Irradiated to 10 Mrad	1.54
Irradiated to 15 Mrad	0.51
Irradiated to 20 Mrad	0.05
Irradiated to 30 Mrad	0.11

Table 13: POD wear rates for specimens of Example 10 (WIR-AM)

<u>Specimen</u>	<u>Wear Rate (mg/million cycle)</u>
Unirradiated Control	9.78
Irradiated to 21 Mrad	1.15

The results indicate that the cross-linked UHMWPE has far superior wear resistance than the unirradiated control.

D. Gel Content and Swell Ratio

The samples were cut in cubes of size 2 x 2 x 2 mm³ and kept submerged in xylene at 130°C for a period of 24 hours. An antioxidant (1% N-phenyl-2-naphthylamine) was added to the xylene to prevent degradation of the sample. The swell ratio

and gel content were calculated by measuring the weight of the sample before the experiment, after swelling for 24 hours and after vacuum drying the swollen sample. The results are shown in Tables 14 and 15 for the specimens obtained from Examples 8 and 10.

Table 14: Gel content and swell ratio for specimens of Example 8 (CIR-SM)

<u>Specimen</u>	<u>Gel Content(%)</u>	<u>Swell Ratio</u>
Unirradiated Control	89.7	12.25
Irradiated to 5 Mrad	99.2	4.64
Irradiated to 10 Mrad	99.9	2.48
Irradiated to 20 Mrad	99.0	2.12
Irradiated to 30 Mrad	99.9	2.06

Table 15: Gel content and swell ratio for specimens of Example 10 (WIR-AM)

<u>Specimen</u>	<u>Gel Content(%)</u>	<u>Swell Ratio</u>
Unirradiated Control	89.7	12.25
Irradiated to 21 Mrad	99.9	2.84
Irradiated to 22.5 Mrad	100	2.36

The results show that the swell ratio decreased with increasing absorbed dose indicating an increase in the cross-link density. The gel content increased indicating the formation of a cross-linked structure.

Example 12: Free Radical Concentration for UHMWPE Prepared by Cold Irradiation With and Without Subsequent Melting (CIR-SM)

This example illustrates the effect of melting subsequent to cold irradiation of UHMWPE on the free radical concentration. Electron paramagnetic resonance (EPR) was performed at room temperature on the samples after placing in a nitrogen atmosphere in an air tight quartz tube. The instrument used was the Bruker ESP 300 EPR spectrometer and the tubes used were Taperlok EPR sample tubes (obtained from Wilmad Glass Co., Buena, NJ).

The unirradiated samples did not have any detectable free radicals in them. During the process of irradiation, free radicals are created which can last for at least several years under the appropriate conditions.

The cold-irradiated UHMWPE specimens exhibited a strong

free radical signal when tested with the EPR technique. When the same samples were examined with EPR following a melting cycle, the EPR signal was found to be reduced to undetectable levels. The absence of free radicals in the cold irradiated subsequently melted (recrystallized) UHMWPE sample means that any further oxidative degradation cannot occur via attack on entrapped radicals.

Example 13: Crystallinity and Melting Point at Different Depths for UHMWPE Prepared by Cold Irradiation and Subsequent Melting (CIR-SM)

This example illustrates the crystallinity and melting point at different depths of the cross-linked UHMWPE specimens obtained from Example 8 with 20 Mrad total radiation dose. Samples were taken at various depths from the cross-linked specimen. The crystallinity and the melting point were determined using a Perkin Elmer differential scanning calorimeter as described in Example 10(B). The results are shown in Table 16.

Table 16: DSC at a heating rate of 10°C/min for specimen of Example 8 irradiated to a total dose of 20 Mrad (CIR-SM)

<u>Depth (mm)</u>	<u>Crystallinity(%)</u>	<u>Melting Point(°C)</u>
0-2	53	137
6-8	54	137
9-11	54	137
14-16	34	137
20-22	52	137
26-28	56	137
29-31	52	137
37-40	54	137
Unirradiated Control	59	137

The results indicate that the crystallinity varied as a function of depth away from the surface. The sudden drop in 16 mm is the consequence of the cascade effect. The peak in the absorbed dose was located around 16 mm where the dose level could be as high as 27 Mrad.

Example 14: Comparison of UHMWPE Prepared by CIR-SM Using Melting in Air Versus Melting Under Vacuum

This example illustrates that the oxidation levels of

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UHMWPE pucks prepared by CIR-SM, whether melted in air or under vacuum, are the same as unirradiated pucks at a depth of 3mm below the surface of the pucks.

Conventional UHMWPE ram extruded bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was used. The GUR 415 resin used for the bar stock had a molecular weight of 5,000,000 g/mol and contained 500 ppm of calcium stearate. The bar stock was cut into "hockey puck" shaped cylinders (height 4 cm, diameter 8.5 cm).

Two pucks were irradiated at room temperature with a dose rate of 2.5 Mrad per pass to 17.5 Mrad total absorbed dose as measured on the top surface (e-beam incidence) (AECL, Pinawa, Manitoba, Canada), with a scan width of 30 cm and a conveyor speed of 0.07 cm/sec. The pucks were not packaged and the irradiation was carried out in air. Subsequent to irradiation, one puck was heated under vacuum to 150°C for 2 hours, and the other puck was heated in air to 150°C for 2 hours, so as to attain a state of no detectable residual crystalline content and no detectable residual free radicals. The pucks were then cooled to room temperature at a rate of 5°C/min. The pucks were then analyzed for the degree of oxidation as described in Example 11(A). Table 17 summarizes the results obtained for the degree of oxidation.

Table 17: Degree of oxidation of specimens melted in air versus in vacuum

(A.U.)	Specimen	Post-Melting Environment	Oxidation Degree at various depths		
			20 μ m	100 μ m	3 mm
	Unirradiated Control	N/A	0.01	0.01	0.02
	Irradiated to 17.5 Mrad	Vacuum	0.07	0.05	0.02
	Irradiated to 17.5 Mrad	Air	0.15	0.10	0.01

The results indicated that within 3 mm below the free surfaces the oxidation level in the irradiated UHMWPE specimens dropped to oxidation levels observed in unirradiated control UHMWPE. This was the case independent of post-irradiation melting atmosphere (air or vacuum). Therefore, post-irradiation melting could be done in an air convection oven without oxidizing the core of the irradiated puck.

Example 15: Method of Making UHMWPE Using Cold Irradiation and Subsequent Melting Using Gamma Irradiation (CIR-SM)

5 This example, illustrates a method of making UHMWPE that has a cross-linked structure and has substantially no detectable free radicals, by cold irradiating with gamma-radiation and then melting the UHMWPE.

10 Conventional UHMWPE ram extruded bar stock (Hoescht Celanese GUR 415 bar stock obtained from Westlake Plastics, Lenni, PA) was used. The GUR 415 resin used for the bar stock had a molecular weight of 5,000,000 g/mol and contained 500 ppm of calcium stearate. The bar stock was cut into "hockey puck" shaped cylinders (height 4 cm, diameter 8.5 cm).

15 The pucks were irradiated at room temperature at a dose rate of 0.05 Mrad/minute to 4 Mrad total absorbed dose as measured on the top surface (gamma ray incidence) (Isomedix, Northboro, MA). The pucks were not packaged and irradiation was carried out in air. Subsequent to irradiation, the pucks were
20 heated to 150°C under vacuum for 2 hours so as to melt the polymer and thereby result in the recombination of free radicals leading to substantially no detectable residual free radicals.

25 Example 16: I. Method of Making UHMWPE Using Warm Irradiation and Partial Adiabatic Melting with Subsequent Complete Melting (WIR-AM)

This example illustrates a method of making UHMWPE that has a cross-linked structure, exhibits two distinct melting
30 endotherms in a differential scanning calorimeter (DSC), and has substantially no detectable free radicals, by irradiating UHMWPE that has been heated to below the melting point so as to generate adiabatic partial melting of the UHMWPE and by subsequently melting the UHMWPE.

35 A GUR 4050 bar stock (made from ram extruded Hoescht Celanese GUR 4050 resin obtained from Westlake Plastics, Lenni, PA) was machined into 8.5 cm diameter and 4 cm thick hockey pucks. Twenty-five pucks, 25 aluminum holders and 25 20cm x 20cm fiberglass blankets were preheated to 125°C overnight in an
40 air convection oven. The preheated pucks were each placed in a preheated aluminum holder which was covered by a preheated fiberglass blanket to minimize heat loss to the surroundings

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during irradiation. The pucks were then irradiated in air using a 10 MeV, 1 kW electron beam with a scan width of 30 cm (AECL, Pinawa, Manitoba, Canada). The conveyor speed was 0.07 cm/sec which gave a dose rate of 70 kGy per pass. The pucks were
5 irradiated in two passes under the beam to achieve a total absorbed dose of 140 kGy. For the second pass, the conveyor belt motion was reversed as soon as the pucks were out of the electron beam raster area to avoid any heat loss from the pucks. Following the warm irradiation, 15 pucks were heated to 150°C
10 for 2 hours so as to obtain complete melting of the crystals and substantial elimination of the free radicals.

A. Thermal Properties (DSC) of the specimens prepared in Example 16

15

A Perkin-Elmer DSC 7 was used with an ice water heat sink and a heating and cooling rate of 10°C/min with a continuous nitrogen purge. The crystallinity of the samples obtained from Example 16 was calculated from the weight of the sample and the
20 heat of melting of polyethylene crystals (69.2 cal/gm). The temperature corresponding to the peak of the endotherm was taken as the melting point. In the case of multiple endotherm peaks, multiple melting points were reported.

Table 18 shows the variations obtained in the melting
25 behavior and crystallinity of the polymer as a function of depth away from the e-beam incidence surface. FIG. 8 shows representative DSC melting endotherms obtained at 2 cm below the surface of e-beam incidence obtained both before and after the subsequent melting.

30

Table 18: WIR-AM GUR 4050 barstock, Total dose=140 kGy, 75 kGy/pass

Depth (mm)	T 1st peak after irradiation (°C)	T 2nd peak after irradiation (°C)	T 3rd peak after irradiation (°C)	T 1st peak after subsequent melting (°C)	T 2nd peak after subsequent melting (°C)	Crystallinity after irradiation (%)	Crystallinity after subsequent melting (%)
1.77	109.70	NP	145.10	116.35	139.45	53.11	45.26
5.61	118.00	NP	147.80	117.10	141.60	52.61	45.46
9.31	113.00	NP	146.40	117.30	141.10	50.13	44.42
13.11	113.47	138.07	145.23	116.03	139.83	47.29	43.33
16.89	113.40	137.40	144.80	115.90	139.30	47.68	43.05
20.95	113.70	138.33	145.17	115.17	139.63	44.99	43.41
24.60	112.40	134.20	143.90	114.90	138.70	49.05	44.40
28.57	112.30	NP	145.70	115.90	139.90	50.84	44.40
31.89	111.20	NP	144.50	114.90	138.80	51.88	45.28
34.95	NP	NP	143.90	112.00	138.45	50.09	45.36
39.02	NP	NP	139.65	114.95	138.30	49.13	46.03

*NP: The peak is not present

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These results indicate that the melting behavior of UHMWPE changes drastically after the subsequent melting step in this embodiment of the WIR-AM process. Before the subsequent melting, the polymer exhibited three melting peaks, while after subsequent melting it exhibited two melting peaks.

B. Electron Paramagnetic Resonance (EPR) of the specimens prepared in Example 16

EPR was performed at room temperature on samples obtained from Example 16 after placing the samples in an air tight quartz tube in a nitrogen atmosphere. The instrument used was the Bruker ESP 300 EPR spectrometer and the tubes used were Taperlok EPR sample tubes (obtained from Wilmad Glass Co., Buena, NJ).

The unirradiated samples did not have any detectable free radicals in them. During the process of irradiation, free radicals are created which can last for at least several years under the appropriate conditions.

Before the subsequent melting, the EPR results showed a complex free radical peak composed of both peroxy and primary free radicals. After the subsequent melting the EPR free radical signal was reduced to undetectable levels. These results indicated that the free radicals induced by the irradiation process were substantially eliminated after the subsequent melting step. Thus, the UHMWPE was highly resistant to oxidation.

Example 17: II. Method of Making UHMWPE Using Warm Irradiation and Partial Adiabatic Melting with Subsequent Complete Melting (WIR-AM)

This example illustrates a method of making UHMWPE that has a cross-linked structure, exhibits two distinct melting endotherms in DSC, and has substantially no detectable free radicals, by irradiating UHMWPE that has been heated to below the melting point so as to generate the adiabatic partial melting of the UHMWPE and by subsequently melting the UHMWPE.

A GUR 4020 bar stock (made from ram extruded Hoescht Celanese GUR 4020 resin obtained from Westlake Plastics, Lenni, PA) was machined into 8.5 cm diameter and 4 cm thick hockey pucks. Twenty-five pucks, 25 aluminum holders and 25 20cm x 20cm fiberglass blankets were preheated to 125°C overnight in an

air convection oven. The preheated pucks were each placed in a preheated aluminum holder which was covered by a preheated fiberglass blanket to minimize heat loss to the surroundings during irradiation. The pucks were then irradiated in air using
5 a 10 MeV, 1 kW electron beam with a scan width of 30 cm (AECL, Pinawa, Manitoba, Canada). The conveyor speed was 0.07 cm/sec which gave a dose rate of 70 kGy per pass. The pucks were irradiated in two passes under the beam to achieve a total absorbed dose of 140 kGy. For the second pass, the conveyor
10 belt motion was reversed as soon as the pucks were out of the electron beam raster area to avoid any heat loss from the pucks. Following the warm irradiation, 15 pucks were heated to 150°C for 2 hours so as to obtain complete melting of the crystals and substantial elimination of the free radicals.

15

Example 18: III. Method of Making UHMWPE Using Warm
Irradiation and Partial Adiabatic Melting with
Subsequent Complete Melting (WIR-AM)

20 This example illustrates a method of making UHMWPE that has a cross-linked structure, exhibits two distinct melting endotherms in DSC, and has substantially no detectable free radicals, by irradiating UHMWPE that has been heated to below the melting point so as to generate adiabatic partial melting of
25 the UHMWPE and by subsequently melting the UHMWPE.

A GUR 1050 bar stock (made from ram-extruded Hoescht Celanese GUR 1050 resin obtained from Westlake Plastics, Lenni, PA) was machined into 8.5 cm diameter and 4 cm thick hockey pucks. Eighteen pucks, 18 aluminum holders and 18 20cm x 20cm
30 fiberglass blankets were preheated to 125°C, 90°C, or 70°C, in an air convection oven overnight. Six pucks were used for each different pre-heat temperature. The preheated pucks were each placed in a preheated aluminum holder which was covered by a preheated fiberglass blanket to minimize heat loss to the
35 surroundings during irradiation. The pucks were then irradiated in air using a 10 MeV and 1 kW electron beam with a scan width of 30 cm (AECL, Pinawa, Manitoba, Canada). The conveyer speed was 0.06 cm/sec which gave a dose rate of 75 kGy per pass. The pucks were irradiated in two passes under the beam to accumulate
40 a total of 150 kGy of absorbed dose. For the second pass, the

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conveyor belt motion was reversed as soon as the pucks were out of the electron beam raster area to avoid any heat loss from the pucks. Following the warm irradiation, half of the pucks were heated to 150°C for 2 hours so as to obtain complete melting of the crystals and substantial elimination of the free radicals.

A. Thermal Properties of the Specimens Prepared in Example 18

10 A Perkin-Elmer DSC 7 was used with an ice water heat sink and a heating and cooling rate of 10°C/min with a continuous nitrogen purge. The crystallinity of the samples obtained from Example 18 was calculated from the weight of the sample and the heat of melting of polyethylene crystals (69.2 cal/gm). The
15 temperature corresponding to the peak of the endotherm was taken as the melting point. In the case of multiple endotherm peaks, multiple melting points were reported.

Table 19 shows the effect of pre-heat temperature on the melting behavior and crystallinity of the polymer. FIG. 9 shows
20 the DSC profile of a puck processed with the WIR-AM method at a pre-heat temperature of 125°C both before and after subsequent melting.

These results indicate that the melting behavior of UHMWPE changes drastically after the subsequent melting step in this embodiment of the WIR-AM process. Before the subsequent melting, the polymer exhibited three melting peaks, while after subsequent melting it exhibited two melting peaks.

Example 19: IV. Method of Making UHMWPE Using Warm Irradiation and Partial Adiabatic Melting with Subsequent Complete Melting (WIR-AM)

10 This example illustrates a method of making UHMWPE that has a cross-linked structure, exhibits two distinct melting endotherms in DSC, and has substantially no detectable free radicals, by irradiating UHMWPE that has been heated to below
15 the melting point so as to generate adiabatic partial melting of the UHMWPE and by subsequently melting the polymer.

A GUR 1020 bar stock (made from ram extruded Hoescht Celanese GUR 1020 resin obtained from Westlake Plastics, Lenni, PA) was machined in 7.5 cm diameter and 4 cm thick hockey pucks.
20 Ten pucks, 10 aluminum holders and 10 20cm x 20cm fiberglass blankets were preheated to 125°C overnight in an air convection oven. The preheated pucks were each placed in a preheated aluminum holder which was covered by a preheated fiberglass blanket to minimize heat loss to the surroundings during
25 irradiation. The pucks were then irradiated in air using a 10 MeV, 1 kW linear electron beam accelerator (AECL, Pinawa, Manitoba, Canada). The scan width and the conveyor speed was adjusted to achieve the desired dose rate per pass. The pucks were then irradiated to 61, 70, 80, 100, 140, and 160 kGy of
30 total absorbed dose. For 61, 70, 80 kGy absorbed dose, the irradiation was completed in one pass; while for 100, 140, and 160 it was completed in two passes. For each absorbed dose level, six pucks were irradiated. During the two pass experiments, for the second pass, the conveyor belt motion was
35 reversed as soon as the pucks were out of the electron beam raster area to avoid any heat loss from the pucks. Following the irradiation, half of the pucks were heated to 150°C for 2 hours in an air convection oven so as to obtain complete melting of the crystals and substantial elimination of the free
40 radicals.

Example 20: V. Method of Making UHMWPE Using Warm Irradiation and Partial Adiabatic Melting with Subsequent Complete Melting (WIR-AM)

5 This example illustrates a method of making UHMWPE that has a cross-linked structure, exhibits two distinct melting endotherms in DSC, and has substantially no detectable free radicals, by irradiating UHMWPE that has been heated to below the melting point so as to generate adiabatic partial melting of
10 the UHMWPE and by subsequently melting the polymer.

 A GUR 4150 bar stock (made from ram extruded Hoescht Celanese GUR 4150 resin obtained from Westlake Plastics, Lenni, PA) was machined into 7.5 cm diameter and 4 cm thick hockey pucks. Ten pucks, 10 aluminum holders and 10 20cm x 20cm
15 fiberglass blankets were preheated to 125°C overnight in an air convection oven. The preheated pucks were each placed in a preheated aluminum holder which was covered by a preheated fiberglass blanket to minimize heat loss to the surroundings during irradiation. The pucks were then irradiated in air using
20 a 10 MeV, 1 kW linear electron beam accelerator (AECL, Pinawa, Manitoba, Canada). The scan width and the conveyor speed was adjusted to achieve the desired dose rate per pass. The pucks were irradiated to 61, 70, 80, 100, 140, and 160 kGy of total absorbed dose. For each absorbed dose level, six pucks were
25 irradiated. For 61, 70, 80 kGy absorbed dose, the irradiation was completed in one pass; for 100, 140 and 160 kGy, it was completed in two passes.

 Following the irradiation, three pucks out of each different absorbed dose level were heated to 150°C for 2 hours
30 to completely melt the crystals and reduce the concentration of free radicals to undetectable levels.

A. Properties of the Specimens Prepared in Example 20

 A Perkin-Elmer DSC 7 was used with an ice water heat sink
35 and a heating and cooling rate of 10°C per minute with a continuous nitrogen purge. The crystallinity of the samples obtained from Example 20 was calculated from the weight of the sample and the heat of melting of polyethylene crystals (69.2 cal/gm). The temperature corresponding to the peak of the
40 endotherm was taken as the melting point. In the case of

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multiple endotherm peaks, multiple melting points were reported.

The results obtained are shown in Table 20 as a function of total absorbed dose level. They indicate that crystallinity decreases with increasing dose level. At the absorbed dose
5 levels studied, the polymer exhibited two melting peaks ($T_1 =$
 $\sim 118^\circ\text{C}$, $T_2 = \sim 137^\circ\text{C}$) after the subsequent melting step.

Irradiation dose (kGy)	T 1st peak after irradiation (°C)	T 2nd peak after irradiation (°C)	T 3rd peak after irradiation (°C)	T 1st peak after subsequent melting (°C)	T 2nd peak after subsequent melting (°C)	Crystallinity after irradiation (%)	Crystallinity after subsequent melting (%)
160	113.4	135.10	143.20	114	135.90	41.97	39.58
140	114.6	135.10	143.60	116.2	138.60	45.25	41.51
100	118.7	125.10	143.50	118.2	138.20	47.18	42.58
80	115.7	NP	142.00	119.1	137.60	50.61	44.52
70	114.8	NP	141.40	118.9	137.00	52.36	44.95
61	114.6	NP	140.20	119.1	136.00	53.01	45.04

NP: The peak is not present

*NP: The peak is not present

Example 21: Temperature Rise during WIR-AM Process

This example demonstrates that the temperature rises during the warm irradiation process leading to adiabatic partial or complete melting of the UHMWPE.

5 A GUR 4150 bar stock (made from ram extruded Hoescht Celanese GUR 4150 resin obtained from Westlake Plastics, Lenni, PA) was machined into a 8.5 cm diameter and 4 cm thick hockey puck. One hole was drilled into the body-center of the puck. A Type K thermocouple was placed in this hole. The puck was pre-
10 heated to 130°C in air convection oven. The puck was then irradiated using 10 MeV, 1 kW electron beam (AECL, Pinawa, Manitoba, Canada). The irradiation was carried out in air with a scan width of 30 cm. The dose rate was 27 kGy/min and the puck was left stationary under the beam. The temperature of the
15 puck was constantly measured during irradiation.

FIG. 11 shows the temperature rise in the puck obtained during the irradiation process. Initially, the temperature is at the pre-heat temperature (130°C). As soon as the beam is turned on, the temperature increases, during which time the
20 UHMWPE crystals melt. There is melting of smaller size crystals starting from 130°C, indicating that partial melting occurs during the heating. At around 145°C where there is an abrupt change in the heating behavior, complete melting is achieved. After that point, temperature continues to rise in the molten
25 material.

This example demonstrates that during the WIR-AM process, the absorbed dose level (duration of irradiation) can be adjusted to either partially or completely melt the polymer. In the former case, the melting can be completed with an additional
30 melting step in an oven to eliminate the free radicals.

Example 22: Method of Making UHMWPE Using Cold Irradiation and Adiabatic Heating with Subsequent Complete Melting (CIR-AM)

35 This example illustrates a method of making UHMWPE that has a cross-linked structure, and has substantially no detectable free radicals, by irradiating UHMWPE at a high enough dose rate to generate adiabatic heating of the UHMWPE and by subsequently
40 melting the polymer.

A GUR 4150 bar stock (made from ram extruded Hoescht Celanese GUR 4150 resin obtained from Westlake Plastics, Lenni, PA) was machined into 8.5 cm diameter and 4 cm thick hockey pucks. Twelve pucks were irradiated stationary, in air, at a dose rate of 60 kGy/min using 10 MeV, 30 kW electrons (E-Beam Services, Cranbury, NJ). Six of the pucks were irradiated to a total dose of 170 kGy, while the other six were irradiated to a total dose of 200 kGy. At the end of the irradiation the temperature of the pucks was greater than 100°C.

Following the irradiation, one puck of each series was heated to 150°C for 2 hours to melt all the crystals and reduce the concentration of free radicals to undetectable levels.

A. Thermal Properties of the Specimens Prepared in Example 22

A Perkin-Elmer DSC 7 was used with an ice water heat sink and a heating and cooling rate of 10°C per minute with a continuous nitrogen purge. The crystallinity of the samples obtained from Example 22 was calculated from the weight of the sample and the heat of melting of polyethylene crystals (69.2 cal/gm). The temperature corresponding to the peak of the endotherm was taken as the melting point.

Table 21 summarizes the effect of total absorbed dose on the thermal properties of CIR-AM UHMWPE both before and after the subsequent melting process. The results obtained indicate one single melting peak both before and after the subsequent melting step.

<u>Table 21: CIR-AM GUR 4150 barstock</u>				
Irradiation dose (kGy)	T peak after irradiation (°C)	T peak after subsequent melting (°C)	Crystallinity after irradiation (%)	Crystallinity after subsequent melting (%)
170	143.67	137.07	58.25	45.27
200	143.83	136.73	54.74	43.28

Example 23: Comparison of Tensile Deformation Behavior of Unirradiated UHMWPE, Cold-Irradiated and Subsequently Melted UHMWPE (CIR-SM), and Warm Irradiated and Partially Adiabatic Melted and Subsequently Melted UHMWPE (WIR-AM)

This example compares the tensile deformation behavior of UHMWPE in its unirradiated form, and irradiated forms via CIR-SM and WIR-AM methods.

The ASTM D638 Type V standard was used to prepare dog bone specimens for the tensile test. The tensile test was carried out on an Instron 4120 Universal Tester at a cross-head speed of 10 mm/min. The engineering stress-strain behavior was calculated from the load-displacement data following ASTM D638.

The dog bone specimens were machined from GUR 4150 hockey pucks (made from ram extruded Hoescht Celanese GUR 4150 resin obtained from Westlake Plastics, Lenni, PA) that were treated by CIR-SM and WIR-AM methods. For the CIR-SM, the method described in Example 8 was followed, while for WIR-AM, the method described in Example 17 was followed. In both cases, the total dose administered was 150 kGy.

FIG. 12 shows the tensile behavior obtained for the unirradiated control, CIR-SM treated, and WIR-AM treated specimens. It shows the variation in tensile deformation behavior in CIR-SM and WIR-AM treated UHMWPE, even though in both methods the irradiation was carried out to 150 kGy. This difference is due to the two phase structure generated by using the WIR-AM method.

Those skilled in the art will be able to ascertain using no more than routine experimentation, many equivalents of the specific embodiments of the invention described herein. These and all other equivalents are intended to be encompassed by the following claims.

CLAIMS

1. A medical prosthesis for use within the body, said prosthesis being formed of radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals.

2. The prosthesis of claim 1 wherein said radiation is selected from the group consisting of gamma radiation and electron radiation.

3. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene has a cross-linked structure, so as to reduce production of particles from said prosthesis during wear of said prosthesis.

4. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene is substantially not oxidized.

5. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene is substantially oxidation resistant.

6. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene has three melting peaks.

7. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene has two melting peaks.

8. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene has one melting peak.

9. The prosthesis of claim 1 wherein said polymeric structure has extensive cross-linking so that a substantial portion of said polymeric structure does not dissolve in xylene at 130°C or decalin at 150°C over a period of 24 hours.

10. The prosthesis of claim 1 wherein said ultra high molecular weight polyethylene has an initial average molecular weight of greater than about 2 million.

11. The prosthesis of claim 1 wherein part of said prosthesis is in the form of a cup or tray shaped article having a load bearing surface.

12. The prosthesis of claim 9 wherein said load bearing surface is in contact with a second part of said prosthesis having a mating load bearing surface of a metallic or ceramic material.

13. The prosthesis of claim 1 wherein said prosthesis is constructed and arranged for replacement of a joint selected from the group consisting of a hip joint, a knee joint, an elbow joint, a shoulder joint, an ankle joint and a finger joint.

14. The medical prosthesis of claim 1 wherein said ultra high molecular weight polyethylene has a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus, so as to reduce production of fine particles from said prosthesis during wear of said prosthesis.

15. The prosthesis of claim 14 wherein said ultra high molecular weight polyethylene has a hardness of less than about 65 on the Shore D scale.

16. The prosthesis of claim 14 wherein said ultra high molecular weight polyethylene has a high density of entanglement so as to cause the formation of imperfect crystals and reduce crystallinity.

17. The prosthesis of claim 14 wherein said ultra high molecular weight polyethylene has a polymeric structure with about 40% crystallinity, about 100Å lamellar thickness and about 200 MPa tensile elastic modulus.

18. Radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals.

19. The ultra high molecular weight polyethylene of claim

18 wherein said ultra high molecular weight polyethylene has a cross-linked structure.

20. The ultra high molecular weight polyethylene of claim
5 18 wherein said ultra high molecular weight polyethylene is substantially oxidation resistant.

21. The ultra high molecular weight polyethylene of claim
18 wherein said ultra high molecular weight polyethylene has
10 three melting peaks.

22. The ultra high molecular weight polyethylene of claim
18 wherein said ultra high molecular weight polyethylene has two
melting peaks.

15

23. The ultra high molecular weight polyethylene of claim
18 wherein said ultra high molecular weight polyethylene has one
melting peak.

20

24. The ultra high molecular weight polyethylene of claim
18 wherein said ultra high molecular weight polyethylene has a
unique polymeric structure characterized by less than about 50%
crystallinity, less than about 290Å lamellar thickness and less
than about 940 MPa tensile elastic modulus.

25

25. The ultra high molecular weight polyethylene of claim
24 wherein said ultra high molecular weight polyethylene has
high transmissivity of light.

30

26. The ultra high molecular weight polyethylene of claim
24 wherein said ultra high molecular weight polyethylene is a
film or sheet, said film or sheet being transparent and wear
resistant.

35

27. A fabricated article formed of radiation treated ultra
high molecular weight polyethylene having substantially no
detectable free radicals.

28. The fabricated article of claim 26 wherein said ultra

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high molecular weight polyethylene has a cross-linked structure.

29. The fabricated article of claim 26 wherein said ultra high molecular weight polyethylene is substantially oxidation
5 resistant.

30. The fabricated article of claim 27 wherein said ultra high molecular weight polyethylene has three melting peaks.

10 31. The fabricated article of claim 27 wherein said ultra high molecular weight polyethylene has two melting peaks.

32. The fabricated article of claim 27 wherein said ultra high molecular weight polyethylene has one melting peak.

15

33. The fabricated article of claim 27 wherein said fabricated article is in the form of a bar stock capable of being shaped into a second article by machining.

20 34. The fabricated article of claim 27 wherein said fabricated article has a load bearing surface.

35. The fabricated article of claim 27 wherein said ultra high molecular weight polyethylene has a polymeric structure
25 with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus.

36. A method for making a cross-linked ultra high
30 molecular weight polyethylene having substantially no detectable free radicals, comprising the steps of:

providing conventional ultra high molecular weight polyethylene having polymeric chains;

irradiating said ultra high molecular weight polyethylene
35 so as to cross-link said polymeric chains;

heating said irradiated ultra high molecular weight polyethylene above the melting temperature of said ultra high molecular weight polyethylene so that there are substantially no detectable free radicals in said ultra high molecular weight

polyethylene; and

cooling said heated ultra high molecular weight
polyethylene to room temperature.

5 37. The method of claim 36 further comprising the step of
machining said cooled ultra high molecular weight polyethylene.

38. The method of claim 37 further comprising the step of
sterilizing said machined ultra high molecular weight
10 polyethylene.

39. The method of claim 36 wherein said ultra high
molecular weight polyethylene in said providing step is selected
from the group consisting of a bar stock, a shaped bar stock, a
15 coating and a fabricated article.

40. The method of claim 36 wherein said ultra high
molecular weight polyethylene in said providing step is a cup or
tray shaped article for use in a prosthesis.

20 41. The method of claim 36 wherein said ultra high
molecular weight polyethylene in said providing step is machined
bar stock.

25 42. The method of claim 36 wherein said ultra high
molecular weight polyethylene in said providing step has an
initial average molecular weight of greater than about 2
million.

30 43. The method of claim 36 wherein said ultra high
molecular weight polyethylene in said providing step is
pre-heated to a temperature below the melting temperature of
said ultra high molecular weight polyethylene.

35 44. The method of claim 43 wherein said pre-heated
temperature of said ultra high molecular weight polyethylene is
about 20°C to about 135°C.

45. The method of claim 43 wherein said pre-heated

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temperature of said ultra high molecular weight polyethylene is about 50°C.

46. The method of claim 43 wherein said pre-heating is
5 done in a non-inert environment.

47. The method of claim 43 wherein said pre-heating is done in an inert environment.

10 48. The method of claim 43 wherein the irradiation is by electron irradiation and the dose rate from said irradiation is about 0.05 to about 10 Mrad/minute.

15 49. The method of claim 43 wherein the irradiation is by electron irradiation and the dose rate from said irradiation is about 4 to about 5 Mrad/minute.

20 50. The method of claim 43 wherein the irradiation is by gamma irradiation and the dose rate from said irradiation is about 0.05 to about 0.2 Mrad/minute.

51. The method of claim 43 wherein said irradiating step is done in an inert environment.

25 52. The method of claim 43 wherein said irradiating step is done in a non-inert environment.

30 53. The method of claim 43 wherein said ultra high molecular weight polyethylene in said providing step is in an insulating material so as to reduce heat loss from said UHMWPE during processing.

54. The method of claim 43 wherein said pre-heated temperature of said ultra high molecular weight polyethylene
35 prior to said irradiating step is about 100°C to about 135°C.

55. The method of claim 43 wherein said pre-heated temperature of said ultra high molecular weight polyethylene prior to the irradiating step is about 120°C.

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56. The method of claim 43 wherein the final temperature of said ultra high molecular weight polyethylene after said heating step is above the melting temperature of said ultra high molecular weight polyethylene.

5

57. The method of claim 56 wherein said final temperature is about 140°C to about 200°C.

58. The method of claim 56 wherein said final temperature
10 is about 145°C to about 190°C.

59. The method of claim 56 wherein said final temperature is about 150°C.

15 60. The method of claim 43 wherein said irradiating step uses electron irradiation so as to generate adiabatic heating.

61. The method of claim 60 wherein said heating of said irradiated ultra high molecular weight polyethylene step results
20 from said adiabatic heating.

62. The method of claim 61 further comprising additionally heating said irradiated ultra high molecular weight polyethylene subsequent to said adiabatic heating so that the final
25 temperature of said ultra high molecular weight polyethylene after said additional heating is above the melting temperature of said ultra high molecular weight polyethylene.

63. The method of claim 62 wherein said final temperature
30 of said ultra high molecular weight polyethylene after said additional heating is about 140°C to about 200°C.

64. The method of claim 62 wherein said final temperature of said ultra high molecular weight polyethylene after said
35 additional heating is about 145°C to about 190°C.

65. The method of claim 62 wherein said final temperature of said ultra high molecular weight polyethylene after said additional heating is about 150°C.

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66. The method of claim 60 wherein the dose rate of said electron irradiation is about 2 to about 3,000 Mrad/minute.

67. The method of claim 60 wherein the dose rate of said
5 electron irradiation is about 7 to about 25 Mrad/minute.

68. The method of claim 60 wherein the dose rate of said electron irradiation is about 7 Mrad/minute.

10 69. The method of claim 60 wherein the total absorbed dose of said electron irradiation is about 1 to about 100 Mrad.

70. The method of claim 60 wherein the total absorbed dose of said electron irradiation is about 22 Mrad.

15

71. The method of claim 36 wherein said ultra high molecular weight polyethylene in said providing step is at room temperature or below room temperature.

20 72. The method of claim 71 wherein said irradiating step uses electron irradiation so as to generate adiabatic heating.

73. The method of claim 72 wherein said heating of said irradiated ultra high molecular weight polyethylene results from
25 said adiabatic heating.

74. The method of claim 73 further comprising additionally heating said irradiated ultra high molecular weight polyethylene subsequent to said adiabatic heating so that the final
30 temperature of said ultra high molecular weight polyethylene after said additional heating is above the melting temperature of said ultra high molecular weight polyethylene.

75. The method of claim 36 wherein said irradiating step
35 is done in a non-inert environment.

76. The method of claim 36 wherein said irradiating step is done in an inert environment.

77. The method of claim 36 wherein said irradiating step uses irradiation selected from the group consisting of gamma irradiation and electron irradiation.

5 78. The method of claim 36 wherein said irradiating step is at a dose rate that does not generate enough heat to melt said ultra high molecular weight polyethylene.

10 79. The method of claim 36 wherein said irradiating step uses gamma irradiation and the dose rate of said gamma irradiation is about 0.005 to about 0.2 Mrad/minute.

15 80. The method of claim 36 wherein said irradiating step uses electron irradiation and the dose rate of said electron irradiation is about 0.05 to about 3,000 Mrad/minute.

81. The method of claim 36 wherein the dose rate from said irradiating step is about 0.05 to about 5 Mrad/minute.

20 82. The method of claim 36 wherein said irradiating step uses electron irradiation and the energy of the electrons is about 0.5 MeV to about 12 MeV.

25 83. The method of claim 36 wherein the total absorbed dose of said irradiation is about 0.5 to about 1,000 Mrad.

84. The method of claim 36 wherein the total absorbed dose of said irradiation is about 1 to about 100 Mrad.

30 85. The method of claim 36 wherein the total absorbed dose of said irradiation is about 4 to about 30 Mrad.

86. The method of claim 36 wherein the total absorbed dose of said irradiation is about 20 Mrad.

35

87. The method of claim 36 wherein the total absorbed dose of said irradiation is about 15 Mrad.

88. The method of claim 36 wherein said temperature in

said heating step is about 137°C to about 300°C.

89. The method of claim 36 wherein said temperature in said heating step is about 140°C to about 300°C.

5

90. The method of claim 36 wherein said temperature in said heating step is about 145°C to about 300°C.

91. The method of claim 36 wherein said temperature in
10 said heating step is about 140°C to about 190°C.

92. The method of claim 36 wherein said temperature in said heating step is about 145°C to about 190°C.

15 93. The method of claim 36 wherein said temperature in said heating step is about 150°C.

94. The method of claim 36 wherein said temperature in said heating step is maintained for about 0.5 minutes to about
20 24 hours.

95. The method of claim 36 wherein said temperature in said heating step is maintained for about 1 hour to about 3
25 hours.

96. The method of claim 36 wherein said heating step is performed in an environment selected from the group consisting of air, an inert gas, a sensitizing atmosphere and a vacuum.

30 97. The method of claim 36 wherein said cooling step is at a rate greater than about 0.1°C/minute.

98. The product made in accordance with claim 36.

35 99. A method for making crosslinked ultra high molecular weight polyethylene, comprising the steps of:

providing conventional ultra high molecular weight polyethylene;

heating said ultra high molecular weight polyethylene above

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the melting temperature of said ultra high molecular weight polyethylene so as to completely melt all crystalline structure of said ultra high molecular weight polyethylene;

5 irradiating said heated ultra high molecular weight polyethylene; and

cooling said irradiated ultra high molecular weight polyethylene to about 25°C.

10 100. The method of claim 99 further comprising surrounding said ultra high molecular weight polyethylene with an inert material that is substantially free of oxygen.

15 101. The method of claim 99 wherein said cooled irradiated ultra high molecular weight polyethylene has substantially no detectable free radicals.

20 102. The method of claim 99 wherein said ultra high molecular weight polyethylene in said providing step is selected from the group consisting of a bar stock, a shaped bar stock, a coating and a fabricated article.

25 103. The method of claim 99 wherein said ultra high molecular weight polyethylene in said providing step is a cup or tray shaped article for use in a prosthesis.

104. The method of claim 99 wherein said ultra high molecular weight polyethylene in said providing step is machined bar stock.

30 105. The method of claim 99 wherein said ultra high molecular weight polyethylene in said providing step has an initial average molecular weight of greater than about 2 million.

35 106. The method of claim 99 wherein said temperature in said heating step is about 145°C to about 230°C.

107. The method of claim 99 wherein said temperature in said heating step is about 175°C to about 200°C.

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108. The method of claim 99 wherein said temperature in said heating step is maintained for about 5 minutes to about 3 hours.

5 109. The method of claim 99 wherein said irradiating step uses irradiation selected from the group consisting of gamma irradiation and electron irradiation.

10 110. The method of claim 99 wherein said irradiating step delivers a dose of greater than about 1 MRad to said heated ultra high molecular weight polyethylene.

111. The method of claim 99 wherein said cooling step is at a rate greater than about 0.5°C/min.

15 112. The method of claim 99 further comprising the step of machining said cooled ultra high molecular weight polyethylene.

20 113. The product made in accordance with claim 99.

114. A method for making highly entangled and crosslinked ultra high molecular weight polyethylene, comprising the steps of:

25 providing conventional ultra high molecular weight polyethylene;

heating said ultra high molecular weight polyethylene above the melting temperature of said ultra high molecular weight polyethylene for a time sufficient to enable the formation of entangled polymer chains in said ultra high molecular weight polyethylene;

30 irradiating said heated ultra high molecular weight polyethylene so as to trap the polymer chains in the entangled state; and

cooling said irradiated ultra high molecular weight polyethylene to about 25°C.

115. The method of claim 114 further comprising surrounding said ultra high molecular weight polyethylene with an inert material that is substantially free of oxygen.

116. The product made in accordance with claim 114.

117. A method of making a medical prosthesis from radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals, said prosthesis resulting in the reduced production of particles from said prosthesis during wear of said prosthesis, comprising the steps of:

providing radiation treated ultra high molecular weight polyethylene having no detectable free radicals; and

forming a medical prosthesis from said ultra high molecular weight polyethylene so as to reduce production of particles from said prosthesis during wear of said prosthesis, said ultra high molecular weight polyethylene forming a load bearing surface of said prosthesis.

118. The method of claim 117 wherein said ultra high molecular weight polyethylene has a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus.

119. A method of treating a body in need of a medical prosthesis, comprising:

providing a shaped medical prosthesis formed of radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals; and

applying said prosthesis to said body in need of said prosthesis.

120. The method of claim 119 wherein said ultra high molecular weight polyethylene has a polymeric structure with less than about 50% crystallinity, less than about 290Å lamellar thickness and less than about 940 MPa tensile elastic modulus.

121. The method of claim 119 wherein said ultra high molecular weight polyethylene has three melting peaks.

122. The method of claim 119 wherein said ultra high molecular weight polyethylene has two melting peaks.

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123. The method of claim 119 wherein said ultra high molecular weight polyethylene has one melting peak.

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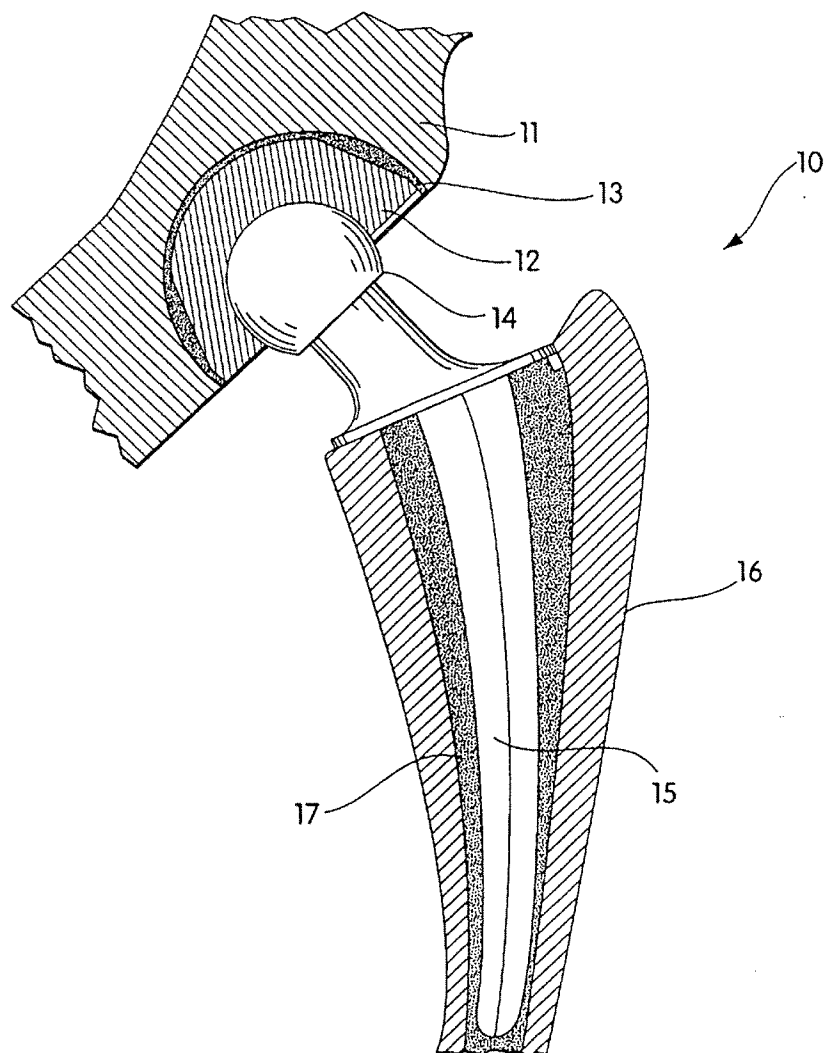


Fig. 1

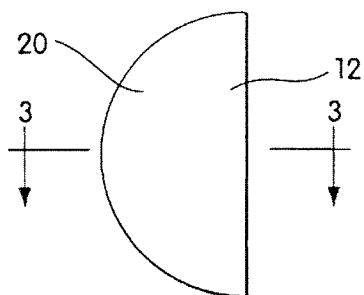


Fig. 2

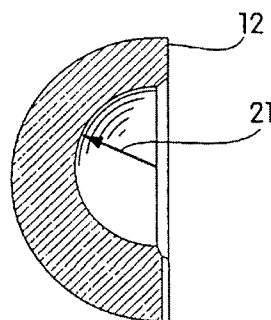


Fig. 3

2/5

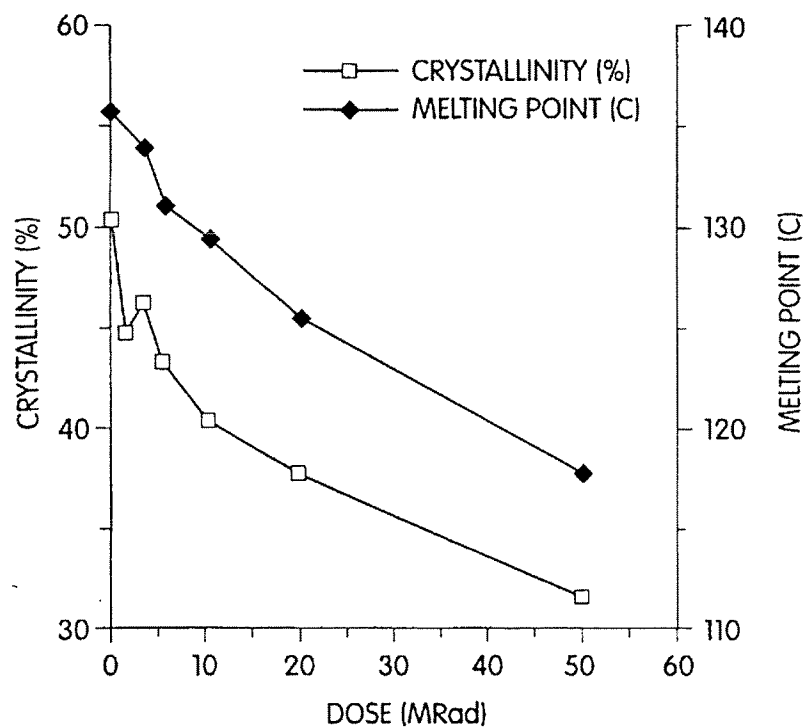


Fig. 4

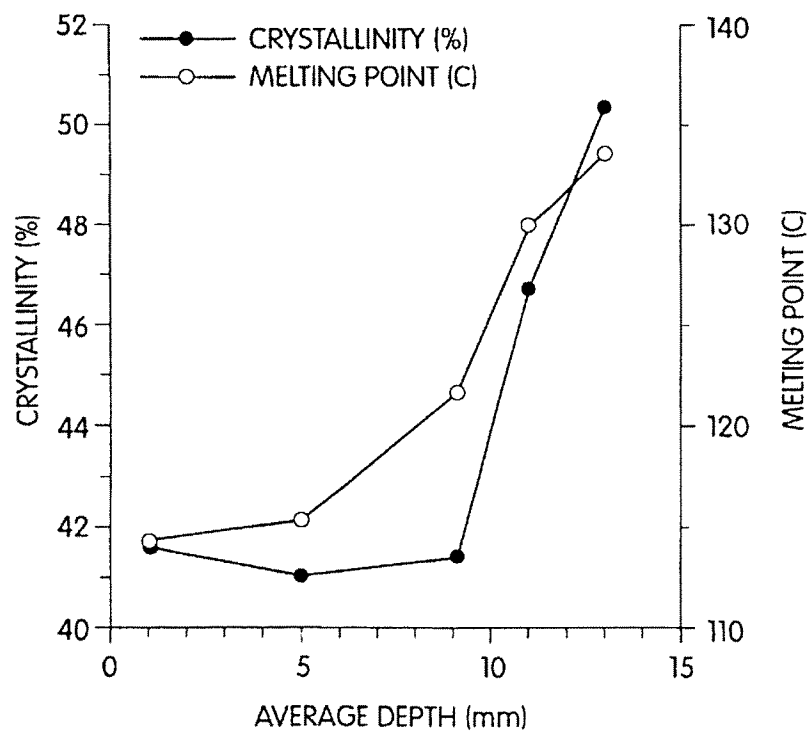


Fig. 7

SUBSTITUTE SHEET (RULE 26)



Fig. 5

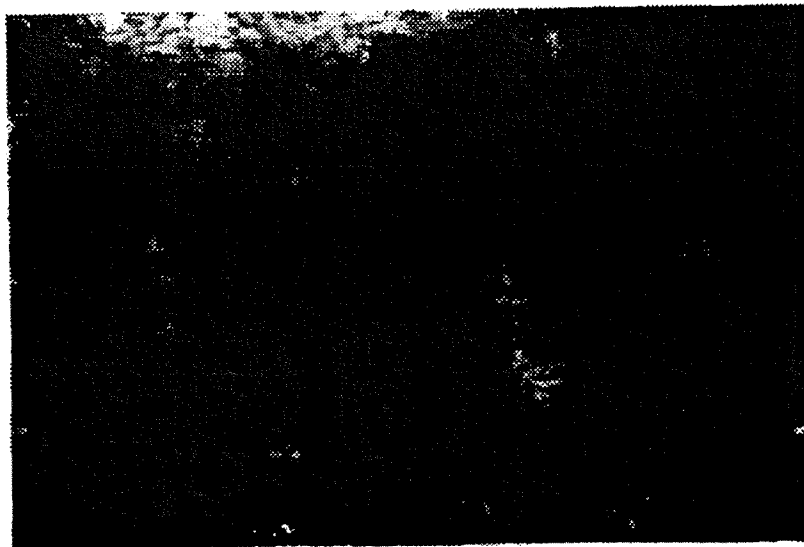


Fig. 6

4/5

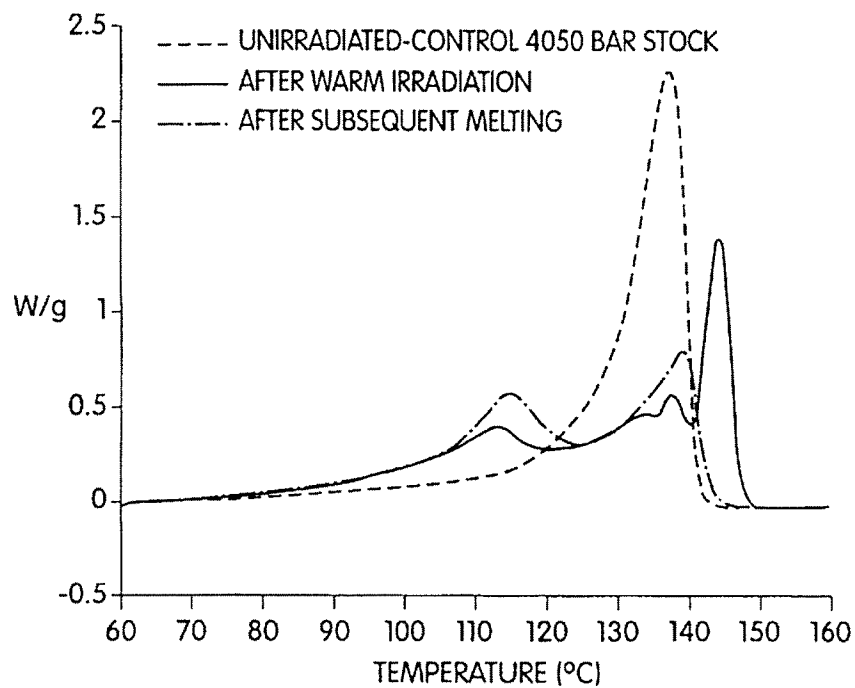


Fig. 8

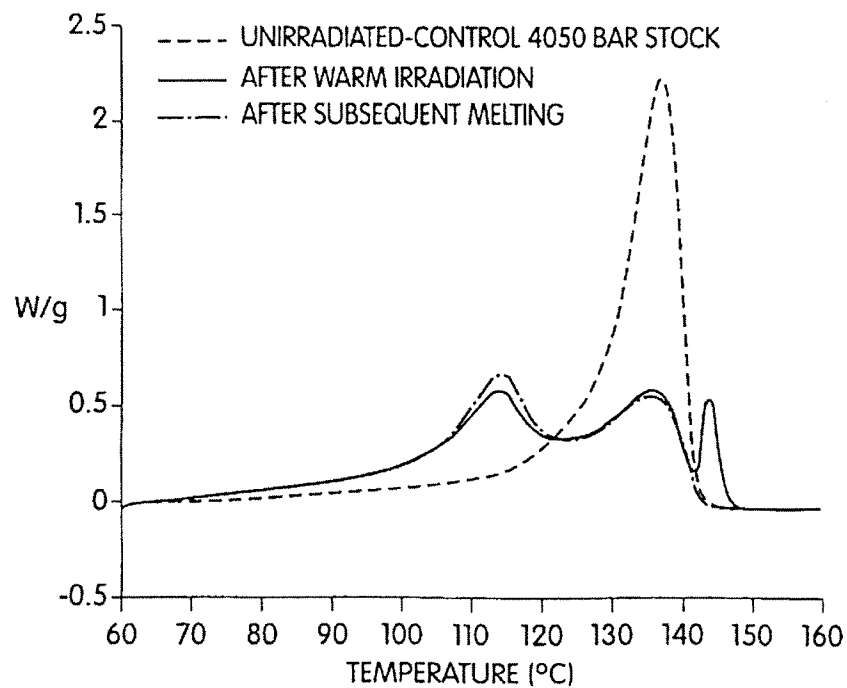


Fig. 9

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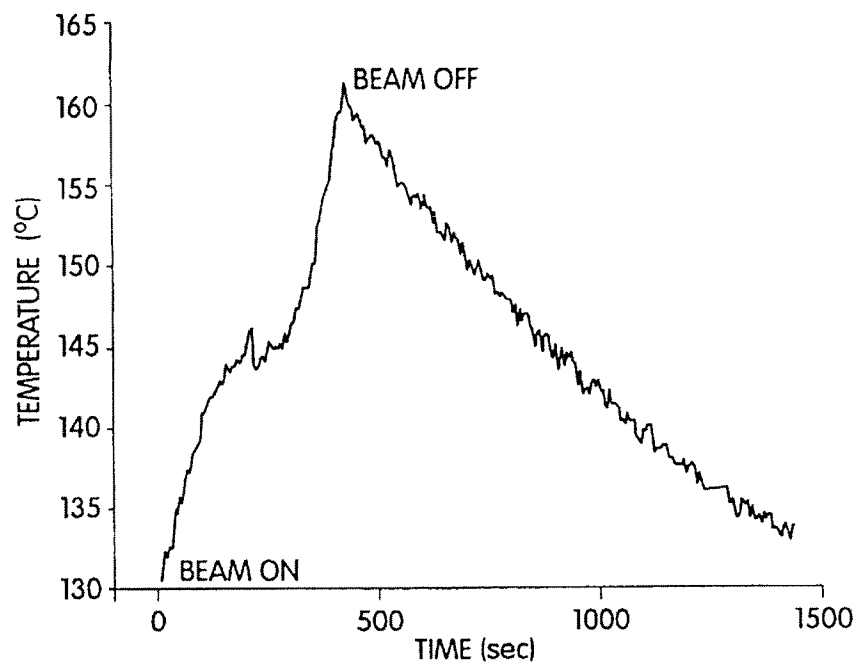


Fig. 10

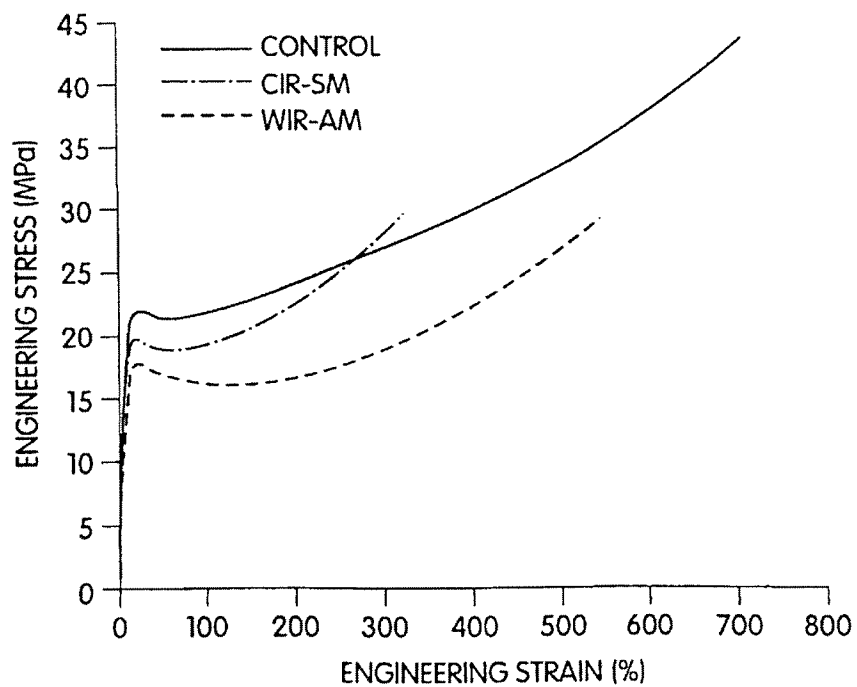


Fig. 11

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/02220

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61L27/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER, vol. 30, no. 5, 1 May 1989, pages 866-873, XP000569234 DIJKSTRA D J ET AL: "CROSS-LINKING OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE IN THE MELT BY MEANS OF ELECTRON BEAM IRRADIATION" see abstract ---	1-5
X	DATABASE WPI Section Ch, Week 8343 Derwent Publications Ltd., London, GB; Class A17, AN 83-798721 XP002034379 & JP 58 157 830 A (NITTO ELECTRIC IND CO) , 20 September 1983 see abstract --- -/--	1-5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

3 July 1997

Date of mailing of the international search report

16. 07. 97

Name and mailing address of the ISA

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Fax (+31-70) 340-3016

Authorized officer

ESPINOSA, M

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 97/02220

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 729 981 A (BMG INC) 4 September 1996 see the whole document ---	1-123
P,X	EP 0 722 973 A (UNIV SOUTHERN CALIFORNIA ;ORTHOPAEDIC HOSPITAL (US)) 24 July 1996 see the whole document ---	1-123
P,X	EP 0 737 481 A (JOHNSON & JOHNSON PROFESSIONAL) 16 October 1996 see claims ---	1-5
A	EP 0 373 800 A (DU PONT) 20 June 1990 see claims ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 501 (C-0996), 16 October 1992 & JP 04 185651 A (FUJIKURA LTD), 2 July 1992, see abstract ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 528 (C-1001), 29 October 1992 & JP 04 198242 A (KOMATSU LTD), 17 July 1992, see abstract -----	1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/ 02220

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
Remark: Although claim(s) 119-123
is(are) directed to a method of treatment of the human/animal
body, the search has been carried out and based on the alleged
effects of the compound/composition.
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such
an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all
searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment
of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report
covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is
restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

(information on patent family members)

International Application No

PCT/US 97/02220

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0729981 A	04-09-96	AU 3485595 A CN 1135762 A WO 9609330 A	09-04-96 13-11-96 28-03-96
EP 0722973 A	24-07-96	AU 4078596 A CA 2166450 A JP 9003207 A	01-08-96 21-07-96 07-01-97
EP 0737481 A	16-10-96	US 5577368 A AU 5046796 A CA 2173279 A JP 8336585 A	26-11-96 17-10-96 04-10-96 24-12-96
EP 0373800 A	20-06-90	AT 138810 T CA 2004454 A DE 68926624 D DE 68926624 T DK 57795 A DK 171157 B EP 0446300 A ES 2087147 T JP 4502028 T WO 9006139 A US 5478906 A US 5621070 A	15-06-96 02-06-90 11-07-96 02-10-96 19-05-95 08-07-96 18-09-91 16-07-96 09-04-92 14-06-90 26-12-95 15-04-97

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VERSION*

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61F 2/00, 2/32, 2/34, C08J 3/28, 5/16, C08F 110/02, 110/06		A1	(11) International Publication Number: WO 98/01085 (43) International Publication Date: 15 January 1998 (15.01.98)
(21) International Application Number: PCT/US97/11947 (22) International Filing Date: 8 July 1997 (08.07.97) (30) Priority Data: 60/017,852 9 July 1996 (09.07.96) US 60/025,712 10 September 1996 (10.09.96) US Not furnished 29 April 1997 (29.04.97) US (60) Parent Applications or Grants (63) Related by Continuation US 60/017,852 (CIP) Filed on 9 July 1996 (09.07.96) US 60/025,712 (CIP) Filed on 10 September 1996 (10.09.96) US Not furnished (CIP) Filed on 29 April 1997 (29.04.97) (71) Applicants (for all designated States except US): THE ORTHOPAEDIC HOSPITAL [US/US]; 2400 South Flower Street, Los Angeles, CA 90007-2693 (US). THE UNIVERSITY OF SOUTHERN CALIFORNIA [US/US]; University Park Campus, Los Angeles, CA 90089 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only): SHEN, Fu-Wen [--/US]; 20308 Trails End Road, Walnut, CA 91789 (US). MCKEL-LOP, Harry, A. [US/US]; 826 South Sierra Bonita Avenue, Los Angeles, CA 90036 (US). SALOVEY, Ronald [US/US]; 6641 Monero Drive, Rancho Palos Verdes, CA 90275 (US). (74) Agents: WETHERELL, John, R. et al.; Fish & Richardson P.C., Suite 1400, 4225 Executive Square, La Jolla, CA 92037 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: CROSSLINKING OF POLYETHYLENE FOR LOW WEAR USING RADIATION AND THERMAL TREATMENTS			
(57) Abstract <p>The present invention discloses methods for enhancing the wear-resistance of polymers, the resulting polymers, and <i>in vivo</i> implants made from such polymers. One aspect of this invention presents a method whereby a polymer is irradiated, preferably with gamma radiation, then thermally treated, such as by remelting or annealing. The resulting polymeric composition preferably has its most oxidized surface layer removed. Another aspect of the invention presents a general method for optimizing the wear resistance and desirable physical and/or chemical properties of a polymer by crosslinking and thermally treating it. The resulting polymeric composition is wear-resistant and may be fabricated into an <i>in vivo</i> implant.</p>			

*(Referred to in PCT Gazette No. 20/1998, Section II)

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CROSSLINKING OF POLYETHYLENE FOR LOW WEAR
USING RADIATION AND THERMAL TREATMENTS

10 This application is based on U.S. provisional applica-
tions: serial number 60/017,852 filed on July 9, 1996;
serial number 60/025,712 filed on September 10, 1996; and
U.S. provisional application, "Crosslinking of Polyethylene
for Low Wear Using Radiation and Thermal Treatments", of Fu-
15 Wen Shen et al., with attorney docket number 5910-108P3
(correct serial number not yet assigned), filed on April 29,
1997.

Technical Field Of The Invention

20 The present invention relates to polymers. It dis-
closes methods for enhancing the wear-resistance of polymers
by crosslinking and thermally treating them. The polymers
disclosed herein are useful for making implants, for exam-
ple, as components of artificial joints such as acetabular
25 cups.

Background Of The Invention

30 Ultrahigh molecular weight polyethylene (hereinafter
referred to as "UHMWPE") is commonly used to make prosthetic
joints such as artificial hip joints. In recent years, it
has become increasingly apparent that tissue necrosis and
interface osteolysis, in response to UHMWPE wear debris, are
primary contributors to the long-term loosening failure of
prosthetic joints. For example, wear of acetabular cups of
35 UHMWPE in artificial hip joints introduces many microscopic
wear particles into the surrounding tissues. The reaction

to these particles includes inflammation and deterioration of the tissues, particularly the bone to which the prosthesis is anchored. Eventually, the prosthesis becomes painfully loose and must be replaced.

Improving the wear resistance of the UHMWPE socket and, thereby, reducing the rate of production of wear debris would extend the useful life of artificial joints and permit them to be used successfully in younger patients. Consequently, numerous modifications in physical properties of UHMWPE have been proposed to improve its wear resistance.

UHMWPE components are known to undergo a spontaneous, post-fabrication increase in crystallinity and changes in other physical properties. {See e.g., Rimnac, C.M., et al., J. Bone & Joint Surgery, 76-A(7):1052-1056 (1994)}. These changes occur even in stored (non-implanted) cups after sterilization with gamma radiation, which initiates an ongoing process of chain scission, crosslinking, and oxidation or peroxidation involving the free radicals formed by the irradiation. These degradative changes may be accelerated by oxidative attack from the joint fluid and cyclic stresses applied during use.

In an attempt to improve wear resistance, DePuy-DuPont Orthopaedics fabricated acetabular cups from conventionally extruded bar stock that previously had been subjected to heating and hydrostatic pressure that reduced fusion defects and increased the crystallinity, density, stiffness, hardness, yield strength, and increased the resistance to creep, oxidation and fatigue. Alternatively, silane cross-linked UHMWPE (XLP) has also been used to make acetabular cups for total hip replacements in goats. In this case, the number of in vivo debris particles appeared to be greater for XLP than conventional UHMWPE cup implants {Ferris, B.D., J. Exp. Path., 71:367-373 (1990)}.

Other modifications of UHMWPE have included: (a) reinforcement with carbon fibers; and (b) post-processing treat-

ments such as solid phase compression molding. Indeed, carbon fiber reinforced polyethylene and a heat-pressed polyethylene have shown relatively poor wear resistance when used as the tibial components of total knee prosthesis. {See e.g., Rimnac, C.M., et al., Trans. Orthopaedic Research Society, 17:330 (1992)}.

Recently, several companies have modified the method of radiation sterilization to improve the wear resistance of UHMWPE components. This has typically involved packaging the polyethylene cups either in an inert gas (e.g., Howmedica, Inc.), in a partial vacuum (e.g., Johnson & Johnson, Inc.) or with an oxygen scavenger (e.g., Sulzer Orthopaedics, Inc.).

Summary Of the Invention

The present invention comprises two aspects:

The first aspect of the invention presents a method for increasing the wear resistance of a polymer by crosslinking the polymer, followed by thermally treating the crosslinked polymer. Non-limiting examples of the thermal treatments are remelting or annealing. Preferably, the polymer is crosslinked by gamma irradiation in the solid state prior to being modified to a desired final form or shape of the final product. In the preferred embodiment, the surface layer of the crosslinked and thermally treated polymer, which is the most oxidized and least crosslinked part of the polymer, is removed, e.g., in the process of machining the final product out of the irradiated bar and thermally treated bar or block. The radiation dose is also preferably adjusted so that the optimal dose occurs within the solid polymer bar or block at the level of the bearing surface of the final product. Also presented are the polymers made from this method; methods for making products (e.g., in vivo implants) from these polymers; and the products (e.g., in vivo implants) made from these polymers.

20 The second aspect of the invention provides a systematic method for determining an optimal balance among wear resistance and other physical and/or chemical properties that are deemed important to the long-term performance of an implant in vivo, and applying this optimal balance to determine the appropriate crosslinking and thermal treatment
25 conditions for processing a polymer. A flowchart is provided as a non-limiting illustration of the method for determining the optimal balance. Also provided are methods for treating polymers which apply the above appropriate crosslinking and thermal treatment conditions; the polymers produced by these
30 methods; methods for making products (e.g., in vivo implants) from these polymers; and the products (e.g., in vivo implants) made from these polymers.

Brief Description Of The Drawings

35 FIG. 1 presents the degree of crystallinity vs. depth at indicated doses for UHMWPE that was irradiated in a vacuum (i.e., a low-oxygen atmosphere).

FIG. 2 presents the gel content vs. depth at indicated doses for UHMWPE that was irradiated in a vacuum (i.e., a
40 low-oxygen atmosphere).

FIG. 3 presents the gel content vs. depth at indicated conditions for UHMWPE.

FIG. 4 presents the degree of crystallinity vs. depth at indicated conditions for UHMWPE.

45 FIG. 5 presents the gel content vs. depth at indicated conditions for UHMWPE.

FIG. 6 presents the shape of the acetabular cup fabricated from the irradiated UHMWPE.

FIG. 7 presents a schematic diagram of the hip joint simulator used in the wear tests.
50

FIG. 8 presents the wear by volume loss of each cup of the four materials. Upper curves: 3.3 Mrad; Lower curves: 28 Mrad.

20 FIG. 9 presents the curves of the average volumetric wear and standard deviations of three cups of each material at each interval.

FIG. 10 presents the oxidation profile as a function of depth at various aging times.

25 FIG. 11 presents the oxidation profile as a function of depth at various aging times.

FIG. 12 presents the oxidation profile as a function of depth at various aging times.

FIG. 13 presents the oxidation profile as a function of depth at various aging times.

30 FIG. 14 presents the oxidation profile as a function of depth for various materials. The specimens were stored in air for 5 months and then aged for 20 days at 80°C.

FIG. 15 presents gel content as a function of depth at various aging times.

35 FIG. 16 presents gel content as a function of depth at various aging times.

FIG. 17 presents gel content as a function of depth at various aging times.

40 FIG. 18 presents gel content as a function of depth at various aging times.

FIG. 19 presents the degree of crystallinity as a function of depth after 30 days' aging.

Fig. 20 shows the combined soak-corrected wear for the non-aged and aged cups.

45 Fig. 21 shows the individual wear for cups irradiated at different doses.

Fig. 22 shows the average wear rate versus radiation dose of non-remelted and remelted cups.

50 Figs. 23A and 23B present the flowchart illustrating the optimization method of the present invention.

Fig. 24 graphically shows the oxidation profiles for irradiated and remelted UHMWPE as a function of depth from the UHMWPE bar surface.

20 Fig. 25 graphically shows the tensile strength at yield versus radiation dose of irradiated UHMWPE with or without remelting, and non-irradiated and not remelted UHMWPE.

Fig. 26 graphically shows the tensile strength at break versus radiation dose of irradiated UHMWPE with or without remelting, and non-irradiated and not remelted UHMWPE.

25 Fig. 27 graphically shows the elongation at break versus radiation dose of irradiated UHMWPE with or without remelting, and non-irradiated and not remelted UHMWPE.

Detailed Description Of The Invention

30 Abbreviations used in this application are as follows:

UHMW -- ultra-high molecular weight
UHMWPE -- ultra-high molecular weight polyethylene
HMW -- high molecular weight
HMWPE -- high molecular weight polyethylene

35

The present invention contains two aspects. The first aspect of the invention provides methods for improving the wear resistance of a polymer by crosslinking (preferably the bearing surface of the polymer) and then thermally treating the polymer, and the resulting novel polymer. Preferably, 40 the most oxidized surface of the polymer is also removed. Also presented are the methods for using the polymeric compositions for making products and the resulting products, e.g., in vivo implants. Specific examples of this method are presented in the section: "I. First Aspect of the Inven- 45 tion: Polymeric Compositions with Increased Wear Resis- tance" and "I (A) Further Examples of the First Aspect of the Invention", below.

50 The method of the invention utilizes irradiation for crosslinking a polymer followed by thermal treatment to decrease the free radicals to produce a preformed polymeric composition. The term "preformed polymeric composition" means that the polymeric composition is not in a final

desired shape or form (i.e., not a final product). For example, where the final product of the preformed polymeric composition is an acetabular cup, irradiation and thermal treatment of the polymer could be performed at pre-acetabular cup shape, such as when the preformed polymeric composition is in the form of a solid bar or block.

A second aspect of the invention provides a systematic method (an example of which is illustrated in the flowchart, below) for determining the optimal parameters for the above mentioned crosslinking and thermal treatment. This second aspect provides a method for determining the maximum possible improvement in wear resistance, consistent with keeping the other physical and/or chemical properties within the user's desired limits, with the least amount of trial and error testing. Once the optimal parameters (i.e., crosslinking conditions such as radiation dose when radiation is used to crosslink the polymer, and thermal treatment parameters) are determined by this method, the polymer will then be processed according to the optimal parameters. Thus, this protocol renders the development of a preformed polymeric composition with particular chemical/mechanical characteristics routine without resort to undue experimentation. Also presented are the methods for using the preformed polymeric composition for making products, and the products, e.g., in vivo implants.

In the present invention, the wear resistance of the polymer is improved by crosslinking. The crosslinking can be achieved by various methods known in the art, for example, by irradiation from a gamma radiation source or from an electron beam, or by photocrosslinking. The preferred method for crosslinking the polymer is by gamma irradiation. The polymer is preferably crosslinked in the form of an extruded bar or molded block.

In the preferred method, the crosslinked polymer is subjected to thermal treatment such as by remelting (i.e.,

20 heated above the melting temperature of the crosslinked polymer) or annealing (i.e., heated at below the melting temperature of the crosslinked polymer) to produce the preformed polymeric composition.

25 In the preferred embodiment of both the first and second aspects of the invention, the outer layer of the resulting preformed polymeric composition, which is generally the most oxidized and least crosslinked and, thus, least wear resistant, is removed. For example, the bearing surface of the preformed polymeric composition may be fashioned from inside, e.g., by machining away the surface of the irradiated and thermally treated composition before or 30 during fashioning into the final product, e.g., into an implant. Bearing surfaces are surfaces which are in moving contact with another, e.g., in a sliding, pivoting, or rotating relationship to one another.

35

Choices of Polymers

The polymers are generally polyester, poly(methylmethacrylate), nylon, polycarbonates, and polyhydrocarbons such as polyethylene, and polypropylene. 40 High molecular weight (HMW) and ultra-high molecular weight (UHMW) polymers are preferred, such as HMW polyethylene (HMWPE), UHMW polyethylene (UHMWPE), and UHMW polypropylene. HMW polymers have molecular weights ranging from about 10^5 grams per mole to just below 10^6 . UHMW polymers have molecular weights equal to or higher than 10^6 grams per mole, 45 preferably from 10^6 to about 10^7 . The polymers are generally between about 400,000 grams per mole to about 10,000,000 and are preferably polyolefinic materials.

50 For implants, the preferred polymers are those that are wear resistant and have exceptional chemical resistance. UHMWPE is the most preferred polymer as it is known for these properties and is currently widely used to make acetabular cups for total hip prostheses and components of

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20 other joint replacements. Examples of UHMWPE are those
having molecular weight ranging from about 1 to 8×10^6
grams per mole, examples of which are: GUR 4150 or 4050
(Hoechst-Celanese Corporation, League City, Texas) with a
weight average molecular weight of 5 to 6×10^6 grams per
25 mole; GUR 4130 with a weight average molecular weight of 3
to 4×10^6 ; GUR 4120 or 4020 with a weight average molecular
weight of 3 to 4×10^6 ; RCH 1000 (Hoechst-Celanese
Corp.) with a weight average of molecular weight of 4×10^6
and HiFax 1900 of 2 to 4×10^6 (HiMont, Elkton, Maryland).
Historically, companies which make implants have used
30 polyethylenes such as HIFAX 1900, GUR 4020, GUR 4120 and GUR
4150 for making acetabular cups.

Sterilization Methods

35 All polymeric products must be sterilized by a suitable
method prior to implanting in the human body. For the formed
crosslinked and thermally treated polymeric compositions
(i.e., the final products) of the present invention, it is
preferable that the products be sterilized by a non-radia-
tion based method, such as ethylene oxide or gas plasma, in
40 order not to induce additional crosslinking and/or oxidation
of the previously treated preformed polymeric composition.
Compared to radiation sterilization, a non-radiation steril-
ization method has a minor effect on the other important
physical characteristics of the product.

45 Nevertheless, the method can be used in conjunction
with radiation sterilization. If the final products are to
be sterilized by an additional dose of radiation, it is
preferable to take into account the effect of this addi-
tional radiation dose on the wear resistance and other
properties of the polymer, in determining the optimum radia-
50 tion dose used in the initial crosslinking. Furthermore, it
is preferable that the radiation sterilization be done while
the final product (e.g., in vivo implant) is packed in a

20 suitable low-oxygen atmosphere (e.g., in partial vacuum, in an inert gas such as nitrogen, or with an oxygen scavenger included) in order to minimize oxidation of the surface layer of the final product during and after sterilization by irradiation.

25 The dose ranges in this application do not take into account radiation sterilization. If radiation sterilization is used, then the dose ranges may have to be adjusted. Such adjustment can be easily performed using the teachings herein. For example, if after comparing the dose-response curves for wear with those for other important physical or
30 chemical properties, it is determined that the optimal total radiation dose is 8 Mrad, and it is intended to sterilize the polymer with 2.5 Mrad gamma radiation (the minimum industrial standard sterilization dose), then the initial radiation dose (before sterilization) should be 5.5 Mrad,
35 such that the total dose (initial plus sterilization doses) will be 8 Mrad. These calculations are approximate, since the total crosslinking achieved will not be exactly equivalent to a single 8 Mrad dose.

40 Nevertheless, the applicants have discovered that a high level of crosslinking in the surface layer of a polymer markedly reduces the degradative effects of surface oxidation, i.e., that would otherwise occur if a non-pre-crosslinked polymer were irradiated in the presence of oxygen (for example, see Fig. 3).

45

Methods for Characterizing the Polymers

The degree of crystallinity can be determined using methods known in the art, e.g. by differential scanning calorimetry (DSC), which is generally used to assess the
50 crystallinity and melting behavior of a polymer. Wang, X. & Salovey, R., J. App. Polymer Sci., 34:593-599 (1987).

Wide-angle X-ray scattering from the resulting polymer can also be used to further confirm the degree of

20 crystallinity of the polymer, e.g. as described in Spruiell,
J.E., & Clark, E.S., in "Methods of Experimental-Physics",
L. Marton & C. Marton, Eds., Vol. 16, Part B, Academic
Press, New York (1980). Other methods for determining the
degree of crystallinity of the resulting polymer may include
25 Fourier Transform Infrared Spectroscopy {Painter, P.C. et
al., "The Theory Of Vibrational Spectroscopy And Its Appli-
cation To Polymeric Materials", John Wiley and Sons, New
York, U.S.A. (1982)} and density measurement (ASTM D1505-
68). Measurements of the gel content and swelling are gener-
ally used to characterize crosslink distributions in poly-
30 mers, the procedure is described in Ding, Z.Y., et al., J.
Polymer Sci., Polymer Chem., 29:1035-38 (1990). FTIR can
also be used to assess the depth profiles of oxidation as
well as other chemical changes such as unsaturation {Nagy,
E.V., & Li, S., "A Fourier transform infrared technique for
35 the evaluation of polyethylene orthopaedic bearing materi-
als", Trans. Soc. for Biomaterials, 13:109 (1990); Shinde,
A. & Salovey, R., J. Polymer Sci., Polym. Phys. Ed.,
23:1681-1689 (1985)}.

40 Use of Crosslinked Polymers for Implants

Another aspect of the invention presents a process for
making implants using the preformed polymeric composition of
the present invention. The preformed polymeric composition
may be shaped, e.g., machined, into the appropriate implants
45 using methods known in the art. Preferably, the shaping
process, such as machining, removes the oxidized surface of
the composition.

Preformed Polymeric Compositions

50 The preformed polymeric compositions of the present
invention can be used in any situation where a polymer,
especially UHMWPE, is called for, but especially in situa-
tions where high wear resistance is desired. More particu-

20 larly, these preformed polymeric compositions are useful for making implants.

Implants Made of Crosslinked Polymers

25 An important aspect of this invention presents implants that are made with the above preformed polymeric compositions or according to the methods presented herein. In particular, the implants are produced from preformed polymeric composition are UHMW polymers crosslinked by gamma radiation followed by remelting or annealing, removing the oxidized surface layer and then fabricating into a final
30 shape. The preformed polymeric composition of the present invention can be used to make implants for various parts of the body, such as components of a joint in the body. For example, in the hip joints, the preformed polymeric composition can be used to make the acetabular cup, or the insert
35 or liner of the cup, or trunnion bearings (e.g. between the modular head and the stem). In the knee joint, the preformed polymeric composition can be used to make the tibial plateau (femoro-tibial articulation), the patellar button (patello-femoral articulation), and trunnion or other bearing components, depending on the design of the artificial
40 knee joint. In the ankle joint, the preformed polymeric composition can be used to make the talar surface (tibio-talar articulation) and other bearing components. In the elbow joint, the preformed polymeric composition can be used to make the radio-numeral joint, ulno-humeral joint, and
45 other bearing components. In the shoulder joint, the preformed polymeric composition can be used to make the glenoro-humeral articulation, and other bearing components. In the spine, the preformed polymeric composition can be
50 used to make intervertebral disk replacement and facet joint replacement. The preformed polymeric composition can also be made into temporo-mandibular joint (jaw) and finger

20 joints. The above are by way of example, and are not meant to be limiting.

The following discusses the first and second aspects of the invention in more detail.

25 I. First Aspect of the Invention: Polymeric Compositions with Increased Wear Resistance

30 The first aspect of the invention provides preformed polymeric compositions which are wear resistant and useful for making in vivo implants. In this aspect, for polymers in general, and more preferably UHMW and HMW polymers, and most preferably UHMWPE and HMWPE, the irradiation dose is preferably from about 1 to about 100 Mrad, and more preferably, from about 5 to about 25 Mrad, and most preferably from about 5 to about 10 Mrad. This most preferable range is based on achieving what the inventors have determined to be a reasonable balance between improved wear resistance and minimal degradation of other important physical properties.

35 In vivo implants of the present invention, i.e., irradiated within the above dose ranges are expected to function in vivo without mechanical failure. The UHMWPE acetabular cups used by Oonishi et al. [in Radiat. Phys. Chem., 39: 495-504 (1992)] were irradiated to 100 Mrad and functioned in vivo without reported mechanical failure after as long as 26 years of clinical use. Furthermore, it is surprising that, as shown in the EXAMPLES, acetabular cups from the preformed polymeric composition prepared according to the present invention, but irradiated to much less than 100 Mrad, exhibited much higher wear resistance than reported by Oonishi et al.

40 45 50 On the other hand, if a user is primarily concerned with reducing wear, and other physical properties are of secondary concern, then a higher dose than the above stipulated most preferable range (e.g., 5 to 10 Mrad) may be

20 appropriate, or vice versa (as illustrated in the detailed examples in the following section). The optimum radiation dose is preferably based on the dose received at the level of the bearing surface in the final product. Gamma radiation is preferred.

25 The irradiated polymer is then preferably remelted at or above melting temperature of the irradiated polymer, e.g., in air. As used herein, the melting temperature of the crosslinked or irradiated polymer is identified from the peak of the melting endotherm as measured by DSC. Preferably, the remelting temperature is from about the melting
30 temperature of the irradiated polymer to about 100°C to about 160°C above the melting temperature of the irradiated polymer; more preferably from about 40°C to about 80°C above the melting temperature of the irradiated polymer; and most preferably from about 1°C to about 60°C above the melting
35 temperature of the irradiated polymer. For example, in the case of UHMWPE, the remelting temperature is preferably from about 136°C to about 300°C, more preferably from about 136°C to about 250°C, and most preferably from about 136°C to about 200°C. Specific conditions for remelting are described
40 in EXAMPLES 1 and 2, below.

Generally, in practice, the remelting temperature is inversely proportional to the remelting period. The polymer is preferably remelted over a period from about 1 hour to about 2 days, more preferably from about 1 hour to about 1
45 day, and most preferably from about 2 hours to about 12 hours.

Since, depending on the time and temperature applied, annealing can produce less of an effect than remelting on physical properties such as crystallinity, yield strength,
50 and ultimate strength, annealing may be used in place of remelting as a means for reducing the free radicals remaining in the polymer after irradiation crosslinking, in order to maintain these physical properties within limits required

20 by the user. Thermal treatment, such as remelting or annealing, removes free radicals and thereby improves long term wear resistance of the polymer. On the other hand, annealing is slower and thus takes longer than remelting, making it likely to be more expensive in industrial applications.

25 The annealing temperature is preferably from about room temperature to below the melting temperature of the irradiated polymer; more preferably from about 90°C to about 1°C below the melting temperature of the irradiated polymer; and most preferably from about 60°C to about 1°C below the melting temperature of the irradiated polymer. For example,
30 UHMWPE may be annealed at a temperature from about 25°C to about 135°C, preferably from about 50°C to about 135°C, and more preferably from about 80°C to about 135°C. The annealing period is preferably from about 2 hours to about 7 days, and more preferably from about 7 hours to about 5 days, and
35 most preferably from about 10 hours to about 2 days.

Instead of using the above range of radiation dose as a criterion, the appropriate amount of crosslinking may be determined based on the degree of swelling, gel content, or molecular weight between crosslinks after thermal treatment.
40 This alternative is based on the applicant's findings (detailed below) that acetabular cups made from UHMWPE falling within a preferred range of these physical parameters have reduced or non-detectable wear. The ranges of these physical parameters include one or more of the following: a degree of swelling of between about 1.7 to about 5.3; molecular weight
45 between crosslinks of between about 400 to about 8400 g/mol; and a gel content of between about 95% to about 99%. A preferred polymer or final product has one or more, and preferably all, of the above characteristics. These parameters can also be used as starting points in the second
50 aspect of the invention (as illustrated by the flowchart, discussed below) for determining the desired radiation dose to balance the improvement in wear resistance with other

20 desired physical or chemical properties, such as polymer strength or stiffness.

After crosslinking and thermal treatment, preferably, the most oxidized surface of the preformed polymeric composition is removed. The depth profiles of oxidation of the preformed polymeric composition can be determined by methods
25 known in the art, such as FTIR, described above and in EXAMPLES 3 and 6. In general, to remove the most oxidized surface, preferably a minimum of about 0.5 mm to 1.0 mm of the surface of preformed polymeric composition which is exposed to air is removed, e.g. by machining, before or
30 while fashioning the preformed polymeric composition into the final product.

I. (A) Further Examples of the First Aspect of the Invention

As noted above, the most preferable range of dose for crosslinking radiation (i.e., from 5 to 10 Mrad) was based on
35 achieving what the inventors have determined to be a reasonable balance between improved wear resistance and minimal degradation of other important physical properties. The following examples illustrate applications of the present invention with alternative criteria for the optimal dose.
40 These examples use in vivo implants as non-limiting examples of the products, and UHMWPE or HMWPE bar or block as a non-limiting example of a starting material.

In the first example, the user desires to achieve a
45 minimum wear rate of the in vivo implant made from the UHMWPE and HMWPE, and the other physical or chemical properties are important but of lesser concern. In such a case, the user may choose to irradiate the UHMWPE and HMWPE bar or block between about 15 Mrad to about 20 Mrad (as shown by
50 Fig. 22). As discussed in the section "II(b) Application of the Flowchart", below, GUR 4150 is representative of UHMWPE and HMWPE. The irradiated UHMWPE or HMWPE bar or block is further remelted or annealed at a temperature and time

described in "I.First Aspect of the Invention: Polymeric Compositions with Increased Wear Resistance", above.

In a second example, the user may wish to produce an UHMWPE which is as wear resistant as possible while meeting the tensile strength at break (ultimate), tensile strength at yield, and elongation at break criteria of the standard specified by the American Society for Testing and Materials F-648 standard (hereinafter referred to as "ASTM F648") for UHMWPE for in vivo use. The information about this standard can be found in a current issue of the Annual Book of ASTM Standards, Medical Devices and Services, "Standard Specification for Ultra-High-Molecular-Weight Polyethylene Powder and Fabricated Form for Surgical Implants", American Society for Testing and Materials. The method of the second aspect of the present invention (as illustrated by the flowchart) may be used to adjust the crosslinking and thermal treatment parameters to meet any current ASTM F648 criteria.

For example, to meet the 1996 ASTM F648 (F648-96) criteria for Type 1 or 2 UHMWPE, the UHMWPE must have: a tensile strength at break (ultimate) of at least 35 MPa (for Type 1) and 27 MPa (for Type 2) at 23°C and 5.08 cm/min; a tensile strength at yield of at least 21 MPa (Type 1) and 19 MPa (for Type 2) at 23°C, and 5.08 cm/min; and elongation at break of at least 300% at 5.08 cm/min. The test conditions are described in ASTM D638, Type IV (Annual Book of ASTM Standards, American Society for Testing and Materials).

Alternatively, to meet the 1996 ASTM F648 criteria for Type 3 UHMWPE, the UHMWPE must have: a tensile strength at break (ultimate) of at least 27 MPa at 23°C and 5.08 cm/min; a tensile strength at yield of at least 19 MPa at 23°C, and 5.08 cm/min; and elongation at break of at least 250% at 5.08 cm/min.

The plots of mechanical properties vs irradiation dose for GUR 4150 (which is representative of Type 2 UHMWPE) (Figs. 25-27) show that, for all of the radiation

20 doses between 5 to 25 Mrad, the above ASTM F648 criteria for
Types 2 UHMWPE are fulfilled except for the elongation at
break, which crosses the 300 limit at about 6 Mrad. Thus, if
the ASTM F648 criteria are to be met for Types 2 UHMWPE, the
maximum (i.e., the most preferred) gamma radiation dose is
25 about 6 Mrad. As illustrated in the second aspect of the
invention (following section), the corresponding curves of
wear and other physical properties vs. crosslinking dose
could be used to determine the preferred dose range for
other Types of UHMWPE or for other polymers in general.

30 II. Second Aspect of the Invention: Method for Optimizing
Wear Resistance and Desirable Physical and/or Chemical
Characteristics of a Polymeric Composition

35 The second aspect of the invention uses the findings in
this patent application (including those presented in the
"EXAMPLES" section, below) to construct a method which
allows one skilled in the art, to systematically identify
the conditions necessary to routinely produce a polymer with
an optimal balance of wear resistance and physical and/or
40 chemical properties, with minimal additional testing and
minimal trial and error. In one embodiment of this aspect
of the invention, the optimizing method can be schematically
illustrated in a flowchart. Once the optimal conditions have
been determined by this method, the polymer can then be
45 subjected to these conditions for processing.

The present invention is based in part, on the discov-
ery that wear rate decreases with increasing radiation dose,
and there is a maximum dose above which there is little or
no additional improvement in wear, but higher doses might
50 degrade other important physical and/or chemical properties
of the polymer, such as yield or ultimate strength, elonga-
tion to failure, impact strength or fatigue resistance, as
well as increasing the susceptibility to oxidation. Oxida-

tion, in turn, is known to adversely affect one or more of these physical properties, and was shown to occur in the examples below for UHMWPE crosslinked at a dose averaging about 28 Mrad if there had been no thermal treatment. Consequently, a polymer irradiated at a high radiation dose may exhibit improved wear resistance, but its other physical or chemical properties may fall outside of desirable or allowable limits, such as those specified by ASTM F648 for UHMWPE for in vivo use.

The method is also based in part on the discovery that, while other important physical properties (such as crystallinity or elongation to break) may be markedly affected by the amount of thermal treatment (e.g., remelting or annealing) applied to the polymer after irradiation crosslinking, the wear resistance is not markedly affected. This latter discovery permits reducing the amount of additional testing required by the user in order to identify the crosslinking dose which will provide the user's desired balance among wear resistance and other physical properties. This method is useful, e.g., in the case where performed polymeric composition made of UHMWPE is used for making in vivo implants, such as acetabular cups.

II (a) Summary of the Steps of the Optimization Method

Thus, the second aspect of the present invention provides a systematic method for optimizing the balance among wear resistance and other desired physical and/or chemical characteristics of a polymer. The steps in this method are summarized in the non-limiting example of the flowchart of Figs. 23A and 23B. In the flowchart and the following discussion, for ease of discussion, irradiation is used as an example of a crosslinking method, and implant is used as an example of the product that is made from the polymer. However, as discussed elsewhere in this application, other crosslinking methods and products may be used.

20 Step 1: The process typically begins with the polymer in solid form, such as an extruded bar or block.

25 Step 2: The bar is irradiated over a range of doses up to the maximum that is likely to produce a material with the desired wear resistance and physical and/or chemical properties. This irradiation may be done, for example, in the case of gamma radiation by means of a cobalt 60 gamma radiation facility as is presently used for industrial-scale sterilization of implants.

30 Step 3: The irradiated bars are then remelted. Applicants found that remelting of an irradiated polymer would substantially reduce the free radicals produced during irradiation, thus minimizing long-term oxidation and chain scission. By improving the polymeric composition's resistance to long-term oxidation, remelting also improves the polymeric composition's long-term resistance to wear. For further discussion of the subject, see EXAMPLES 2, 3, and 4, below

40 Although the bar may be contained in a low-oxygen atmosphere during the remelting, this may not be essential since, even if the bar is remelted in ambient air, the resultant oxidation may affect only the surface layer of the polymer (e.g. in the following EXAMPLE section, Figs. 2, 5, and 24, show oxidation extending to about 1 mm deep). In the preferred embodiment of the invention, the oxidized surface layer of the preformed polymeric composition will be removed, e.g., during subsequent machining of the products out of the treated bar.

50 Step 4A The radiation dose is correlated with the wear resistance of the products made from the irradiated remelted polymeric composition, as determined in a wear test that

adequately simulates the wear conditions of the products.
20 For example, if the polymeric composition will be made into
an implant, then the wear test should preferably adequately
simulate the wear conditions of such implants in vivo. The
correlation may be arrived at by plotting a dose-response
curve for irradiation dose vs. wear.

25 Step 4B: Similarly, the radiation dose is correlated with
each of the physical and/or chemical properties that may be
markedly affected by the radiation dose and that might, in
turn, substantially affect the performance of the implant in
30 vivo, both for non-remelted and remelted polymer. Again,
the correlation may be arrived at by plotting a dose-re-
sponse curve for irradiation dose vs. each of these physical
and/or chemical properties.

The user does not have to do dose vs. properties for
35 each property that might be affected, but only those proper-
ties that are considered important for the proper function-
ing of the implant in vivo. Which of these properties are
important for the intended application, and the limiting
values of these properties, may vary for different polymeric
40 compositions and for different types of applications (e.g.,
hip prostheses compared to knee prostheses) and must, there-
fore, be established by the user before applying the
flowchart.

45 Step 5 is the first attempt at optimization. The user may
first decide on the desired amount of improvement in the
wear resistance, i.e., the maximum wear rate that is permis-
sible for the user's application. The dose-response curve
for wear (Step 4A) then shows the minimum radiation dose
50 necessary to provide this amount of improvement in wear
resistance.

Similarly, the dose response curves for the other
physical or chemical properties deemed critical or important

20 (Step 4B) provide the values of these properties corresponding to the specific radiation dose identified in Step 4A as being necessary to provide the desired improvement in wear resistance. If each of these other physical or chemical properties are within allowable limits for the crosslinked and remelted polymer, then an optimal method has been identified (Step 6). In other words, the implant can be made by 25 irradiating the solid polymer bar, remelting the bar and machining out the implant; the entire process being conducted such that the resulting implant has received the optimal dose at its bearing surface.

30 Alternatively, the user may first decide on critical values for one or more properties, such as ultimate tensile strength, fatigue strength, etc., and then check the corresponding dose response curves for the remelted polymer for the maximum allowable dose, and then check the wear vs. dose 35 curve to determine whether this dose gives sufficient improvement in wear (i.e., the user does not necessarily have to begin by choosing the desired amount of improvement in wear).

40 However, if not enough improvement in wear will be obtained while keeping these other chemical and physical properties within allowable limits, or conversely, if the dose required for the desired wear improvement causes one or more of these properties to be out of allowable limits, then the user can use a lower radiation dose (i.e., accept a 45 higher wear rate) if he wishes to remelt the materials or, alternatively, annealing may be substituted for remelting (Step 7). For a crosslinked material, annealing is less efficient than remelting in removing free radicals, but may cause less of a reduction in other important physical properties. 50

Whether annealing is a practical option will be apparent from the dose-response curves for the non-remelted and

20 remelted polymers. That is, if the desired value of the property in question falls between the two curves (see for example, Figs. 25 and 26), then a polymer with the desired limiting value may be produced by an annealing process with an appropriate time/temperature combination.

25 It is not necessary to generate additional wear dose-response curves for each of the many possible combinations of annealing time and temperature. It is expected that the radiation dose necessary to produce the desired reduction in wear that is determined from the wear dose-response curve for remelted polymer in Step 4A, will also apply to an
30 annealed polymer produced in Step 7.

Step 7: Anneal samples of a bar or block which have been irradiated to that dose that was identified in Step 4A as being necessary to provide the required improvement in wear
35 resistance, at various time/temperature combinations, to produce a polymer with the critical properties between those for non-remelted and remelted materials.

40 Step 8: The physical or chemical propert(ies) of interest of the irradiated and annealed samples of the polymer are correlated with annealing times and temperatures.

45 Step 9: Using ultimate tensile strength as an example of the physical characteristic of interest, depending on the resultant curve for annealing time and/or temperature vs. ultimate strength, the radiation dose required to achieve the desired wear resistance identified in Step 4A (above) should produce a polymer with an ultimate strength within allowable limits.

50 Similar consideration should be given to each of the other important physical and/or chemical properties by generation of individual curves of these properties versus annealing time and/or temperature. If each of these proper-

20 ties is within allowable limits at a particular annealing time and temperature combination, then a suitable method has been identified (Step 10).

25 If an annealing process cannot be identified that maintains the properties within allowable limits, then the user may choose to accept a lower radiation dose (Step 11), i.e., to accept less of an improvement in wear resistance. However, if a lower radiation dose (and, therefore, a greater wear rate) is acceptable, then the corresponding physical and chemical properties should again be checked for the remelted polymer (using the correlation arrived earlier in Step 4B), since these may be within limits at the lower radiation dose.

30 If the properties are within limits for the remelted polymer at the lower radiation dose, then remelting may be used instead of annealing to produce a polymer with the desired improvement in wear resistance (Step 6). If not, then the user should proceed with annealing as before (Steps 35 7 through 10 or 11) but at this lower radiation dose.

40 The user may wish to progressively reduce the required amount of radiation crosslinking (i.e., to accept still higher wear rate) until a dose is identified for which all of the other properties deemed essential are within the user's required limits. The resultant dose represents the maximum improvement in wear resistance obtainable within the user's criteria.

45

II(b) Example Applications of the Flowchart

50 As starting points for the flowchart, the ranges for radiation doses, remelting and annealing temperatures and times described in section "I. First Aspect of the Invention: Polymeric Compositions with Increased Wear Resistance" and "I (A) Further Examples of the First Aspect of the Invention", above, can be used, with regard to poly-

mers in general, UHMW and HMW polymers in particular, and
20 HMWPE and UHMWPE especially.

For ease of discussion, the following examples illustrate the application of the flowchart using UHMWPE (which also behaves similar to HMWPE) as an example of a polymer and an acetabular cup as an example of an implant. GUR 4150
25 is representative of such a class of UHMWPE. Similarly, the description uses gamma radiation as an example for crosslinking the polymer. These examples are meant to illustrate and not meant to limit the invention.

The method described by the flowchart is applicable to
30 other polymers, implants or other products made from such polymers, and crosslinking methods (examples of which are described elsewhere in this application), and methods for making an implant or product out of the preformed polymeric composition.

From the data provided by the EXAMPLES (following sections) a number of generalities were discovered that allowed simplification of the use of the flowchart, i.e., to minimize the amount of additional testing that would be required of a user wishing to apply the method to other
40 polymers, or to the GUR4150 of the EXAMPLES but with various optimization criteria.

To establish the critical curve for the reduced in vivo wear (Step 4A), the UHMWPE bar or block is preferably irradiated in Step 2 and remelted in Step 3, in a manner and to
45 a dose and temperature and time as described for UHMWPE in the section, "I. First Aspect of the Invention: Polymeric Compositions with Increased Wear Resistance" and "I (A) Further Examples of the First Aspect of the Invention", above.

50 In step 4A, acetabular cups are machined out of the irradiated bar and wear tested under conditions suitably representative of the intended in vivo application (e.g., by the method described in the EXAMPLES section below) to

20 establish a wear vs. radiation dose response curve for the
specific polymer. EXAMPLE 5 and Fig 22 show a wear dose-
response curve for gamma irradiated GUR 4150 UHMWPE.

25 Applicants discovered that it is not necessary to
generate additional wear dose-response curves for each of
the many possible combinations of annealing time and temper-
ature. This follows from the results of EXAMPLE 2. Since
annealing is done at a lower temperature than remelting and,
therefore, has a less marked effect on physical properties
in general, it can be expected that annealing will have even
less of an effect on the wear resistance than remelting.

30 Another important aspect of the invention is the dis-
covery that wear resistance of GUR 4150 was not markedly
affected by remelting and, therefore, it is also not likely
to be markedly affected by annealing time and temperature.
Therefore, it is expected that the radiation dose necessary
35 to produce the desired reduction in wear that is determined
from the wear dose-response curve for remelted polymer in
Step 4A, will also apply to an annealed polymer produced in
Step 7. Therefore, while the user needs to do his own tests
to establish tensile strength vs dose etc., he can rely on
40 the wear vs dose curve developed for the remelted material,
rather than running an additional set of wear curves for
each annealing condition. This represents a considerable
saving in experimental costs, since the tensile strength
tests typically may be completed in a few days (using common
45 tensile test apparatus), but the tests of wear vs dose
require months to complete (and require highly specialized
equipment and techniques available on only a handful of
laboratories in the world).

50 Furthermore, if the user is working with GUR 4150, he
can use the dose vs wear curve of Fig. 22 (as well as the
plots of other mechanical properties, Figs. 25-27) without
needing to run any wear or tensile tests. Finally, if he is
working with another grade of UHMW polyethylene, he can

probably use Fig. 22, since other tests have shown that the wear resistances of these materials are very similar to GUR 4150 for a given sterilization treatment. At the least, Fig. 22 establishes the range on which the user may focus his wear vs. dose experiments for other grades of UHMW polyethylene, to minimize the testing necessary to identify the optimum dose.

For other polymers, comparable wear tests at each end of the range of interest for radiation dose could be applied to verify whether remelting or annealing also does not markedly affect their wear resistance. Nevertheless, GUR 4150 is representative of UHMWPEs, especially those useful for implants, in its physical and chemical properties, and applicants have observed that other UHMWPEs, of different molecular weights and with or without calcium stearate, such as GUR 1020 (calcium stearate free, lower molecular weight grade) behaved similarly to GUR 4150 in their wear resistance after irradiation sterilization in air. McKellop, H. et al., Trans. Society for Biomaterials, Vol. 20, pg. 43 (1997).

Further, it has been observed that, although the starting physical properties of HMWPE are different from those of UHMWPE, these differences will be substantially reduced after sufficient crosslinking. For example, they are almost equal after electron beam irradiation treatment to 300 kGy (30 Mrad), for properties like gel content, swelling and strength. Streicher, R. M., Beta-Gamma 1/89: 34-43, at p. 42, right col., fourth full paragraph. Even the wear properties were the same, after the differences in the molecular arrangement between HMWPE and UHMWPE were offset by the irradiation procedure. Thus, it is predicted that the findings based on GUR 4150 and the above discussion would be applicable to polymers in general, and to UHMW and HMW polymers, in particular, and especially HMWPE and UHMPE. Thus, the radiation, remelting and annealing ranges found

20 for GUR 4150 can be applied to polymers in general, and more preferably to HMW and UHMW polymers, and most preferably to HMWPE and UHMWPE; and these ranges can be used at the very least, as starting points in the flowchart for determining the specific ranges for other polymers, and the data in the "EXAMPLES" section below will facilitate the user in arriving at the proper conditions for GUR 4150, ASTM F648 Type 2 UHMWPE, and UHMWPE and HMWPE in general.

25 The following examples illustrate the use of these generalities in conjunction with the flowchart. In the first example, if the user is working with GUR 4150, or an UHMWPE that satisfies ASTM F648 Type 2 criteria in general, then, based on Figs. 25-27, only the elongation will fall below the ASTM limit (i.e., 300%) over the dose range of interest, i.e., 0 to 25 Mrad, and this occurs at about 6 Mrad. Thus, the maximum allowable dose is 6 Mrad and, from the wear vs dose plot (Fig. 22), it can be seen that a 6 Mrad dose will provide a wear rate of about 7 to 8 mm³ per million cycles. This is about a 78% or more reduction over the 33.1 mm³ per million cycles shown for non-remelted polyethylene gamma irradiated to 3.1 Mrad in air. If this reduction in wear rate is sufficient for the user's purpose, then his goal is achieved. Note however, that the elongation vs dose plot (Fig. 27) shows virtually the same behavior whether the polyethylene is remelted or not, so if the above 78% reduction is not sufficient for the user's purpose, then the user would have no choice but to increase the radiation dose, as annealing is also not likely to affect the elongation to break, for the reasons discussed above.

40 In a second example, a user requires a lower limit on tensile strength at break at 40 MPa, and wishes to produce a material with wear no more than 1 mm³ per million cycles. The wear vs dose curve (Fig. 22) shows that a dose of about 15 Mrad is required to produce a polyethylene with the desired amount of wear resistance. However, the tensile

20 strength at fracture vs dose curve shows that the tensile
strength at 15 Mrad for a remelted material is about 36 Mpa.
Since this is below the user's acceptable limit of 40 Mpa,
he can either use a smaller radiation dose and, therefore,
accept a smaller improvement in wear rate (i.e., if he
25 wishes to remelt his material) or he can try annealing
instead of remelting since, depending on the
time/temperature combination used, annealing can be expected
to produce a polymer with a value of tensile strength be-
tween the limits indicated by the curves for non-remelted
and remelted polymer (Figs. 25 and 26). As shown on these
30 figures, the tensile strength at 15 Mrad for a non-remelted
material is about 46 Mpa, well above the user's limit of 40.
So, with minimal trial and error, the user can identify an
annealing time and temperature that, when applied to a
polyethylene that has been exposed to 15 Mrad radiation, has
35 a tensile strength of the required 40 Mpa. Again, based on
the wear test results, the user knows that he does not have
to re-do the wear vs dose curve for all of the various
annealing treatments he tries, in order to identify the dose
necessary to produce the desired improvement in wear resis-
40 tance.

Having described the invention, the following examples
are presented to illustrate and support the invention, and
are not to be construed as limiting the scope of the inven-
tion.

45

EXAMPLES

50 The nominal dose of radiation applied to implants at a
commercial radiation facility typically varies within a
range. Therefore, in the following examples, the average
gamma radiation doses are given, such as average gamma
radiation doses of 3.3, 26.5, and 28 Mrad. The average of
3.3 Mrad was arrived at by averaging the minimum and maximum

20 doses, e.g., a minimum of 3.28 and a maximum of 3.45 Mrad. Similarly, for example, the average of 26.5 was based on averaging a minimum of 25.14 and a maximum of 27.70 Mrad; and the average of 28 was based on averaging a minimum of 26.01 and a maximum of 30.30 Mrad.

25 EXAMPLE 1: EFFECT OF RADIATION ATMOSPHERE AND DOSE ON THE PHYSICAL PROPERTIES OF UHMWPE

Experimental Details

30 Commercial-grade UHMWPE extruded bars (GUR 4150, Poly Hi Solidur), with a weight average molecular weight of $5-6 \times 10^6$, were used as received. The 8mm thick specimens were cut from the bars and irradiated with gamma-rays at room temperature either in ambient air or in a vacuum chamber at SteriGenics International (Tustin, CA) to average doses
35 ranging from 3.3 to 250 Mrad. Radiation was delivered at a dose rate of 0.2 Mrad/hr. For 250 Mrad, the dose rate was 4 Mrad/hr. Cobalt-60 was used as a source of gamma radiation. A subset of the 8mm thick specimens that had been irradiated in vacuum was remelted in a vacuum oven by heating from room
40 temperature to 145°C slowly (at about 0.3°C/min.) and maintaining at 145°C for one hour. After remelting, the specimens were slowly cooled to room temperature.

The physical properties of the disk specimens before and after irradiation and remelting were characterized by
45 DSC, gel content analysis and FTIR.

Gel Content Analysis

The gel content of each material was analyzed as a function of depth from the surface. 100 μ m thick sections
50 (about 50 mg) were microtomed across the specimen. Extraction of the sol-fraction was performed by boiling in p-xylene for 24 hours, with 0.5 wt% of antioxidant (2,6-di-tert-butyl-4-methyl phenol) added to prevent oxidation. For

highly oxidized sections from the surface layer, which
20 tended to break up during boiling, the specimens were
wrapped in PTFE membrane filter (0.5 μ m pore size) to avoid
loss of gel. After extraction, the specimens were de-swol-
len in acetone and dried at 60°C in a vacuum oven to con-
stant weight. The gel fraction was determined from the
25 ratio of the weight of the dried-extracted material to that
of the dry non-extracted material.

Differential Scanning Calorimetry (DSC)

For DSC measurements, samples were cored and microtomed
30 into 200 μ m thick sections across the depth. Specimens (~4
mg) were heated from 50°C at 10°C/min in a differential
scanning calorimeter (Perkin-Elmer DSC-4) to 170°C. The
melting temperature was identified from the peak of the
melting endotherm. Indium was used for calibration of the
35 temperature and heat of fusion. The heat of fusion was
determined by comparing the area under the melting endotherm
to the area of fusion of an indium sample having a known
heat of fusion of 28.4 J/g, and divided by 292 J/g, the heat
of fusion of an ideal polyethylene crystal, to get the
40 degree of crystallinity.

Results and Discussion

As shown in Fig. 1, irradiation increased the
crystallinity of the 8mm thick specimens of UHMWPE from
45 about 55% to 60-66%, with considerable overlapping for the
different doses. Similar changes were observed with the
samples that were irradiated in air. The gel content (i.e.,
the extent of crosslinking) (Fig. 2) also increased with
increasing radiation dosage. Importantly, crosslinking
50 increased markedly moving from the surface into the middle
of each specimen, reaching about 92% for the 3.3 Mrad dose.
Apparently, the oxygen present in the vacuum chamber was
sufficient to cause the increased oxidation and decreased

crosslinking of the surface layer. Thus, our method, i.e.,
20 of irradiating a bar and machining away the surface is more
effective and efficient than use of a vacuum or other low
oxygen atmosphere in producing a final product with minimal
oxidation of the bearing surface. For reference (Fig. 3),
chemically crosslinked polyethylene (PE) (1% peroxide, irra-
25 diated in air) (Shen, F.W. et al. J. of Poly. Sci. Part B: Poly Phys 34:1063-1077 (1996)), which exhibits very low
wear, has a gel content of about 90% at about 100 microns
from the surface, rising to a maximum of nearly 100% in the
center.

30 In a second phase of this example, the 8mm thick disks
that had been irradiated in vacuum were remelted by heating
to 145°C for one hour, and slowly cooled. This reduced the
peak melting temperature, the degree of crystallinity and
the crystal size. For example (Fig. 4), the crystallinity
35 of the 3.3 Mrad specimens was reduced from the range of 60-
65% to the range of 50-53% by remelting.

In addition, during remelting, residual free radicals
that were formed by the irradiation apparently recombined
and increased the total crosslinking (as evident from the
40 increased gel content, Fig. 5). Extinguishing free radicals
in this manner, in turn, further reduces the oxidation that
would otherwise occur when the cups are stored on the shelf
or exposed to body fluids after implantation.

The lower gel content (crosslinking) near the surface
45 (Fig. 3) was due to oxidation of the surface layer at the
time of irradiation. Thus, it can be expected that the
polymer of the surface layer would have less wear resistance
than that in the center of the specimen. In the method
presented in this application, this gradient would not be
50 present, since the surface layer would be removed during
machining of the final implant from the irradiated bar or
block.

20 The crystallinity and gel content of the irradiated 8mm thick disks, with and without remelting, are compared in Figs. 4 and 5, respectively.

EXAMPLE 2: WEAR TESTING OF RADIATION CROSSLINKED CUPS WITH AND WITHOUT REMELTING

25

Experimental Details

30 Six extruded bars of UHMWPE (GUR 4150), each 3 inches in diameter, were exposed to 3.3 or 28 Mrad of gamma radiation at a dose rate of 0.2 Mrad per hour in ambient air (SteriGenics, Inc., Tustin, CA). Two bars for each radiation dose were then remelted by heating in an oven in ambient atmosphere from room temperature to 150°C at about 0.3°C per minute and holding at 150°C for five hours, and then slow-cooling to room temperature. The crystallinity and gel content of these four materials were measured across the cross section of extra samples of each bar using differential scanning calorimetry (DSC) and gel content analysis. The results are summarized in Tables 1 and 2.

40 Four sets of acetabular cups were machined from bars of each of the four materials at a commercial machining shop (Bradford and Meneghini Manufacturing Co., Santa Fe Springs, CA). Each cup had a 2 inch outer diameter (O.D.) and 1.26 inch inner diameter (I.D.), and 1 inch outer radius and 0.633 inch inner radius (Fig. 6). Wear tests were run on two sets of three cups for each radiation dose that had been remelted, and two sets of three cups for each dose that had not been remelted. The bars were intentionally used with larger diameters than the final cups so that the process of machining away the outer 0.5 inches of each bar removed the most oxidized, most crystalline, least crosslinked surface layer which is about 0.5 to 1.0 mm thick. In this manner, the bearing surface of each cup consisted of material from near the center of the bar, i.e., the most crosslinked,

50

20 least crystalline, least oxidized region, which is predicted to be the most wear resistant.

Since acetabular cups used in patients must first be sterilized by some acceptable means, the test cups in this study were sterilized prior to wear testing using ethylene oxide at the appropriate dose for clinical implants. Ethylene oxide was chosen instead of additional gamma irradiation (e.g., 2.5-4.0 Mrad) in order to confine the results to the effects of the original 3.3 or 28 Mrad doses used to crosslink the materials.

30 Prior to wear testing, the cups were pre-soaked in distilled water for three weeks to minimize additional fluid absorption during the wear test, thereby making the weight loss method for wear measurement more accurate. For the wear test, the cups were enclosed in polyurethane molds and pressed into stainless steel holders (Fig. 7). Each holder was fitted with an acrylic chamber wall to contain the lubricant. The chambers were mounted on the hip simulator wear machine, with each cup bearing against a ball of cobalt-chromium alloy (conventional hip replacement femoral balls were used, with implant-quality surface finish). The ball-cup pairs were subjected to a physiological cyclic load with a peak load of about 2000 Newtons (Paul, JP., "Forces transmitted by joints in the human body". In Lubrication and Wear in Living and Artificial Human Joints. Proc Instn Mech Engrs 1967;181 Part 3J:8-15) and the cups were oscillated against the balls through a bi-axial 46° arc at 68 cycles per minute. Each test station on the simulator (Fig. 7) contains a self-centering unit 5, the acetabular cup 6, a dual axis offset drive block 7, a test chamber 8, serum lubricant 9 and a femoral ball 10. The arrow indicates the direction of the computer controlled simulated physiological load applied to the simulated hip joint.

50 During the test, the bearing surfaces were kept immersed in bovine blood serum to simulate lubrication in the

human body. Sodium azide at 0.2% was added to the serum to
20 retard bacterial degradation, and 20 mM ethylene-
diaminetetraacetic acid (EDTA) was added to prevent precipi-
tation of calcium phosphate onto the surface of the balls
(McKellop, H. and Lu, B., "Friction and Wear of
Polyethylene-metal and Polyethylene-ceramic Hip Prostheses
25 on a Joint Simulator, Transactions of the Fourth World
Biomaterials Congress, Berlin, Apr. 1992, p. 118). A poly-
ethylene skirt covered each test chamber to minimize air-
borne contaminants.

At intervals of 250,000 cycles, the cups were removed
30 from the machine, rinsed, inspected under light microscopy
and replaced in fresh lubricant. At intervals of 500,000
cycles, the cups were removed, cleaned, dried and weighed to
indicate the amount of wear. After inspection under light
microscopy, the cups were replaced on the wear machine with
35 fresh lubricant and testing was continued to a total of
three million cycles. One million cycles is approximately
the equivalent of one year's walking activity of a typical
patient.

The weight loss was corrected for the effects of fluid
40 absorption (which masks wear) by increasing the apparent
weight loss of the wear test cups by the mean weight gain of
three control cups of each material that were also immersed
in serum and cyclically loaded on a separate frame, but
without oscillation. The corrected rate of weight loss was
45 converted to volume loss by dividing by the approximate
density of UHMWPE (0.94 gm/cc). The mean weight loss (after
soak correction) and the standard deviation was calculated
for each of the four types of materials at each weighing
interval. The wear rate of each cup was calculated by
50 applying linear regression to the wear data for the entire
three million cycles. The mean wear rates and standard
deviations also were calculated for each type of material.

Results

20 Fig. 8 shows the soak-corrected wear (volume loss) of
three cups of each material as a function of wear cycles.
Fig. 9 shows the average wear (volume loss) of three cups of
each material as a function of wear cycles. The individual
wear rates and the mean values for each type of material are
25 listed in Table 3. The most wear occurred with the cups
subjected to 3.3 Mrad without remelting. These averaged
21.1 mm³ per million cycles.

The wear of the cups subjected to 3.3 Mrad with remelt-
ing averaged 18.6 mm³ per million cycles, or 12% lower wear
30 than for the non-remelted 3.3 Mrad cups. The cups subjected
to 28 Mrad had much lower wear rates than the 3.3 Mrad cups,
and the rates were similar, whether or not the material had
been remelted. That is, the average wear rate of the non-
remelted 28 Mrad cups was about 1.2% that of the non-re-
35 melted 3.3 Mrad controls, and the average wear rate of the
remelted 28 Mrad cups was about 1.7% of the same controls.

Discussion

The results of the wear test clearly demonstrated the
40 improved wear resistance of the UHMWPE acetabular cups that
resulted from exposure to 28 Mrad gamma radiation. Appar-
ently, the crosslinking generated by the higher radiation
dose reduced the wear rates to less than a few percent of
the control value (3.3 Mrad). The minimum amount of wear
45 debris necessary to induce clinically significant osteolysis
and other problems in a specific patient has not been estab-
lished, and it may vary among patients. Nevertheless, a
material which reduces the wear rate to the very low levels
exhibited by the 28 Mrad cups in this study would be very
50 likely to provide a large margin of safety over currently
used materials.

The wear curves for both of the 28 Mrad specimens
(Figs. 8 & 9) were slightly negative on the first weighing

20 at 0.5 million cycles. This was most likely due to a slight
under-correction for fluid absorption (that is, the wear
test cups absorbed slightly more water than the soak con-
trols, and the error between the two was greater than the
weight loss due to wear, producing a negative wear value).
25 If this assumption is correct, then the overall wear rates
for the two 28 Mrad sets were somewhat smaller, and possibly
closer together, than the values indicated in Table 3.

EXAMPLE 3: ARTIFICIAL AGING OF RADIATION-CROSSLINKED UHMWPE

30

MATERIALS

35 Six UHMWPE (GUR 4150) extruded bars (3" diameter) were
gamma irradiated in air, three bars each at 3.3 or 28 Mrad,
at a dose rate of 0.2 Mrad/hour. For each radiation dose,
two bars were then remelted by heating in an oven at ambient
atmosphere from room temperature to 150°C at about
0.3°C/min, holding at 150°C for 5 hours and slowly cooling
to room temperature, and the third bar was not remelted. A
40 13 mm (0.5 inch) layer of the outer diameter of the treated
(remelted) and untreated (non-remelted) bars was machined
away to remove the most oxidized, least crosslinked surface
layer. The bars were used to produce specimens for the
artificial aging tests described here and for the wear tests
described in EXAMPLE 2.

45 To examine the effect of artificial aging on these four
materials (3.3 and 28 Mrad, remelted and not remelted), 8 mm
thick disks were cut from these 2 inch diameter cores and
were heated in an oven slowly (~ 0.2 °C/min) to 80 °C at
ambient atmosphere and held at 80°C for 10, 20 or 30 days.
50 In addition, one acetabular cup for each of the four condi-
tions (3.3 and 28 Mrad, remelted and not remelted) that had
been fabricated at the same time as the wear test cups of

20 EXAMPLE 2 and stored in air for about 5 months was cut into four pieces and aged at 80°C for the same periods.

The gel content analysis and DSC method are as described in EXAMPLE 1, above.

Fourier Transform Infrared Spectroscopy (FTIR)

25 FTIR measurements were performed on the above specimens. Segments about 5 mm wide were cut from each polyethylene specimen and the segments were microtomed into 200 μm thick slices. The oxidation profiles, as indicated by the carbonyl concentration, were measured using a Mattson Polaris FTIR (model IR 10410) with a Spectra-Tech IR plan
30 microscope. Spectra were collected in 100 μm steps from the surface to the middle of the specimen, using 64 scans summation at a resolution 16 cm^{-1} with a MCT (Mercury Cadmium Telluride) detector. The carbonyl group concentration was
35 indicated by the ratio of the peak height of the ketone absorption band at 1717 cm^{-1} to the height of the reference band at 2022 cm^{-1} (- CH_2 - vibration).

RESULTS

40 The oxidation profiles as a function of depth are shown in Figs. 10-13. As shown in Fig. 10 for the 3.3 Mrad, non-remelted material, oxidation increased with increasing aging time. In contrast, the 3.3 Mrad, remelted material (Fig. 11) showed almost no oxidation for 10 and 20 days aging, but
45 some oxidation for 30 days aging. However, the oxidation peak at the surface with remelting was about 50% of that at the surface without remelting (Fig. 10). For the 28 Mrad, non-remelted UHMWPE (Fig. 12), the oxidation showed a greater increase with increasing aging time than the 3.3
50 Mrad, un-remelted material. Again, oxidation was much lower with remelting, i.e., the 28 Mrad, remelted UHMWPE (Fig. 13) essentially exhibited no oxidation after 20 days aging (Fig.

13), and the oxidation peak at the surface after 30 days was
20 only about 1/3 that without remelting (Fig. 12).

Similarly, with the acetabular cups stored in air for 5
months and then aged for 20 days at 80°C, the remelted
materials (3.3 or 28 Mrad) showed no oxidation (Fig. 14),
while the non-remelted cups (3.3 or 28 Mrad) showed substan-
25 tial oxidation (Fig. 14), especially for 28 Mrad UHMWPE, and
with a subsurface oxidation peak in both non-remelted mate-
rials.

Since crosslinking of UHMWPE reduces its solubility,
the percent of undissolved material (gel content) is an
30 indirect indication of the amount of crosslinking. The gel
content as a function of depth for various conditions are
shown in Figs. 15 to 18. As shown in Fig. 15 for 3.3 Mrad,
non-remelted material, the gel content (i.e., crosslinking)
decreased with increasing aging time. There was a strong
35 gradient of gel content in the highly oxidized surface
regions after 30 days aging, i.e., increasing from a minimum
on the surface to a maximum about 2 mm below the surface.
Near the surface, the gel content was highest (91%) in the
un-aged specimen, and decreased with increasing aging time
40 to less than about 5% in the same region for the 30 day aged
specimen. In contrast, the remelted materials (Fig. 16)
showed much less reduction in gel content in the surface
regions than the non-remelted materials. That is, compari-
son of Fig. 17 (28 Mrad, non-remelted) and Fig. 18 (28 Mrad,
45 remelted) showed that the remelted UHMWPE had much higher
retention of gel content (i.e., crosslinking).

The results of the DSC measurements indicated the
degree of crystallinity as a function of depth for various
materials aged for 30 days at 80°C, as shown in Fig. 19.
50 Near the surface, the degree of crystallinity was 83% for
the 28 Mrad, non-remelted material after aging, compared to
65% before aging. The high level of crystallinity and
increased brittleness of the surface zone of the aged mate-

20 rial often resulted in fragmentation of a layer about 1 mm
thick during microtoming. In contrast, the 28 Mrad remelted
material showed less increase in crystallinity in the sur-
face regions due to aging, and no brittle zone was observed.
Similarly, due to aging, the 3.3 Mrad non-remelted material
25 exhibited an increase in crystallinity from 60% to about
78%, and the surface layer was again brittle, although not
as brittle as with the 28 Mrad, non-remelted material.

DISCUSSION

30 Irradiation of UHMWPE produces crosslinking, chain
scission and the formation of free radicals. If oxygen is
present, it may react with the free radicals to form oxi-
dized species, leading to additional chain scission (reduc-
tion in molecular weight) and an increase in crystallinity.
Since polymer crystallites melt and become amorphous above
35 the melting temperature, molecular chain movements and
rotations are increased, favoring the recombination of free
radicals. The results of the present experiments showed
that remelting at 150°C apparently caused the residual free
radicals to decay and/or to recombine to form crosslinks,
40 leading to an increased gel content. Therefore, remelting
is an effective way to extinguish free radicals, making the
material less susceptible to long-term oxidation and poten-
tially improving the long-term wear resistance, as evident
from the results of the artificial aging experiments, where
45 there was much less oxidation of the remelted materials.

For a crosslinked polymer, oxidative degradation
cleaves the molecules and leads to a reduction in gel con-
tent. This was evident in the present experiments from the
reduced gel content after aging, particularly with the non-
50 remelted materials (Figs. 15 to 18). That is, the distribu-
tion of oxidation, as indicated by the profiles measured by
FTIR, was inverse to the gel content within the material;
the higher the oxidation, the lower the gel content

(crosslinking). Since remelting extinguishes free radicals and increases gel content, thereby reducing the susceptibility to oxidation, the remelted materials (3.3 and 28 Mrad) had a much greater gel content after artificial aging than the non-remelted materials.

An appropriate amount of crosslinking of UHMWPE can improve its wear resistance. The high level of crosslinking in the UHMWPE caused by the 28 Mrad gamma irradiation, as evident from the high gel content (EXAMPLE 2), apparently contributed to the much greater wear resistance exhibited by the acetabular cups tested in EXAMPLE 2. In addition, as shown in EXAMPLE 3, remelting of the irradiated UHMWPE markedly reduced the residual free radicals, rendering the material much more resistant to subsequent oxidation and, therefore, resistant to a reduction in crosslinking, which can be of substantial benefit for implants in long-term clinical use.

EXAMPLE 4: WEAR TESTING OF IRRADIATED CUPS WITH AND WITHOUT ARTIFICIAL AGING

Materials and Methods

The wear testing of irradiated cups with and without remelting was described in EXAMPLE 2. Effects of artificial aging on the physical properties of irradiated UHMWPE, with and without remelting, were described in EXAMPLE 3. To examine the resistance of crosslinked cups to thermal-induced oxidation, and the effect of such oxidation on the wear of irradiated cups with and without remelting, two acetabular cups for each of the four conditions (3.3 and 28 Mrad, remelted and not remelted) that had been wear tested for 3 million cycles as described in EXAMPLE 2, were heated in an oven slowly (~ 0.2 °C/min) to 80 °C at ambient atmosphere and held at 80 °C for 20 days, with one acetabular cup for each of the four conditions being stored in ambient

20 air. The oxidation profile after 20-day aging for each condition was shown in Fig. 14, EXAMPLE 3.

25 Prior to wear testing, the cups were pre-soaked in distilled water for four weeks to minimize additional fluid absorption during the wear test, thereby making the weight loss method for wear measurement more accurate. The details for the wear test were described in EXAMPLE 2.

Results

30 Fig. 20 shows the combined soak-corrected wear (volume loss) for the cups before aging (3.3 and 28 Mrad, remelted and not remelted) during the first 3 million cycles (same data as EXAMPLE 2) and for the same cups, after two cups of each material had been artificially aged, from 3 to 7 million cycles. The individual wear rates and the mean values for each type of material, calculated by linear regression, 35 are listed in Table 4.

40 All cups subjected to 3.3 Mrad with remelting showed comparable wear rates, whether or not the material had been remelted or remelted and aged. Wear was negligible for all of the cups subjected to 28 Mrad, whether or not these were remelted, and whether or not they were aged.

Discussion

45 The results of the wear test clearly demonstrated the improved wear resistance of the UHMWPE acetabular cups that resulted from exposure to 28 Mrad gamma radiation. Apparently, the minor oxidation at the surface (Fig. 14) of the highly crosslinked acetabular cups (28 Mrad, without remelting) induced by the artificial aging, had very limited effect on the wear resistance. Although a substantial oxidation peak occurred about 0.4 mm below the surface, because 50 of the very high wear resistance of the 28 Mrad cups, the total penetration due to wear was too shallow to reach this sub-surface oxidized zone, even after 4 million cycles.

For the non-remelted 3.3 Mrad cups, subsurface oxidation, peaking at about 1 mm below the surface (Fig. 14), occurred after aging in air at 80 °C for 20 days. Since the total depth of penetration of these cups was about 300 microns (at 7 million cycles), the full effect of this subsurface oxidation would not become apparent until a much larger number of wear cycles.

Nevertheless, the sub-surface oxidation in the non-remelted cups (EXAMPLE 3, particularly for the 28 Mrad specimen) leads to reduced molecular weight, a reduction in crosslinking (as indicated by gel content) and an increased crystallinity and brittleness, all of which can contribute to reductions in mechanical properties such as fatigue strength and, eventually, a reduction in wear resistance. Although remelting had no apparent effect on the wear resistance of the aged cups in the present example, the elimination of free radicals by remelting improves the long-term resistance to oxidation, thereby improving the long-term wear resistance *in vivo*.

EXAMPLE 5: WEAR TESTING OF GAMMA-IRRADIATED UHMWPE WITH MULTIPLE DOSES

Materials and Methods

In EXAMPLE 2, we demonstrated the improved wear resistance of UHMWPE acetabular cups that resulted from exposure to 28 Mrad gamma radiation, as compared to cups irradiated to 3.3 Mrad. The average wear rate of the 28 Mrad cups was less than 2% of that of the 3.3 Mrad cups (i.e., a dose within the normal 2.5 to 4.0 Mrad range used to sterilize implants). To examine the wear as a function of radiation dose and, thereby, determine an optimum dose for reducing wear, extruded bars of GUR 4150 UHMWPE, 3" diameter x 15" long, were gamma irradiated in air, three bars at each dose of 4.5, 9.5, 14.5, 20.2 or 24 Mrad (SteriGenics, Inc.,

Corona, CA), at a dose rate of 0.45 Mrad/hour. Additional
20 bars were irradiated in air to 50 or 100 Mrad (SteriGenics
Inc., Tustin, CA), at a dose rate of 0.67 Mrad/hour. For
each radiation dose, two bars were then remelted by heating
in an oven in ambient atmosphere from room temperature to
150 °C at about 0.3 °C/min, holding at 150 °C for 5 hours
25 and then slowly-cooled to room temperature, with the third
bar not being remelted. The irradiated-remelted bars were
used to produce acetabular cups for the wear tests.

Seven sets of acetabular cups were machined from the
irradiated-remelted bars for each of the seven doses at a
30 commercial machining shop (Bradford and Meneghini Manufac-
turing Co., Santa Fe Springs, CA). Each cup had a 2" O.D.
and 1.26" I.D., with 1" outer radius and 0.63" inner radius
(Fig. 6). Wear tests were run on the remelted specimens,
using two cups for each radiation dose from 4.5 to 24 Mrad,
35 and one cup each for 50 and 100 Mrad. The bars were inten-
tionally used with larger diameters than the final cups so
that the process of machining away the outer layer of each
bar, about 0.5 inch thick, effectively removed the most
oxidized, most crystalline, least crosslinked surface layer
40 (about 0.5 to 1.0 mm). In this manner the bearing surface of
each cup consisted of material from near the center of the
bar, i.e., the most crosslinked, least crystalline, least
oxidized region, which was expected to be the most wear
resistant.

45 Because acetabular cups used in patients must first be
sterilized by some acceptable means, the test cups in this
study were sterilized prior to wear testing using ethylene
oxide at the appropriate dose for clinical implants. Ethyl-
ene oxide was chosen instead of additional gamma irradiation
50 (e.g., 2.5-4.0 Mrad) in order to focus the results on the
effects of the radiation doses used to crosslink the materi-
als. Prior to wear testing, the cups were pre-soaked in
distilled water for four weeks to minimize additional fluid

20 absorption during the wear test, thereby making the weight loss method for wear measurement more accurate. The details for the wear test method were described in EXAMPLE 2.

Results

25 Fig. 21 shows the soak-corrected wear (volume loss) of each material (three cups for 3.3 Mrad from EXAMPLE 2, two cups each for radiation dose from 4.5 to 24.5 Mrad, and one cup each for 50 and 100 Mrad). The individual wear rates, determined by linear regression, and the mean values for each type of material are listed in Table 5. At about 2.1 million cycles, there was a temporary overloading of the test cups, due to a malfunction of the computer controller. Although this overload had only a minor effect on the wear rates of the cups, the cup irradiated to 100 Mrad cracked and was, therefore, removed from the test.

35 Fig. 22 shows the average wear rate (volume loss from 1 to 5 million) of each type of material, that had been re-melted (denoted in the figure by darkened circles) and that had not been re-melted (denoted in the figure by an open circle), as a function of dose.

40 The wear of the cups subjected to 3.3 or 4.5 Mrad with remelting averaged 17.5 or 9.3 mm³ per million cycles, respectively, showing about 13% or 54% lower wear than for the 3.3 Mrad non-remelted cups (20.1 mm³ per million cycles). In contrast, the wear rate of the 9.5 Mrad remelted cups averaged 2.2 mm³ per million cycles, i.e., about 89% lower than for the 3.3 Mrad non-remelted cups. For radiation doses greater than 9.5 Mrad, minimal systematic wear occurred, such that, compared to that with 3.3 Mrad non-remelted cups, the wear rates were about 94% lower for the 14.5 Mrad remelted cups, and minimal wear (>99% reduction) for the 20.2 Mrad remelted cups.

50 "Negative" wear rates were calculated for the cups given 24 Mrad or greater doses. Apparently, these cups

20 absorbed more water than the soak control cups, and the error between the two was greater than the weight loss due to wear, giving a net gain in weight.

Discussion

25 The results clearly demonstrated that the wear resistance of UHMWPE acetabular cups were improved substantially with increasing radiation dose over the range of 4.5 to 9.5 Mrad (i.e., with increasing crosslinking), such that wear was too small to accurately quantify for doses exceeding about 20 Mrad. Since, in addition to improving wear resistance,
30 radiation induced crosslinking may degrade other physical properties, such as elongation to failure and fatigue strength, the dose-response curve developed in the present example provides the opportunity to select an optimum dose, i.e., one that provides the desired amount of
35 improvement in wear resistance with a minimum reduction in other physical properties. The procedure for arriving at the choice of dose for a particular in vivo application is described in this application.

40 UHMWPE acetabular cups that had been compression molded and then exposed to 3.1 Mrad gamma radiation in air but were not thermally treated (i.e., typical of commercially used implants over the past two decades), showed an approximate wear rate of 33.1 mm³/million cycle using the procedure of the wear test described in EXAMPLE 2, above. When compared
45 to these conventional UHMWPE acetabular cups, the acetabular cups of the present invention (i.e., irradiated bar stock, remelted and machined into cups) show the following percentage reduction in wear rate: for the 3.3 Mrad remelted acetabular cup from EXAMPLE 2, above (about 47% reduction in
50 wear rate); 4.5 Mrad remelted acetabular cup from EXAMPLE 5, above (about 72% reduction in wear rate); 9.5 Mrad remelted acetabular cup from EXAMPLE 5, above (about 93% reduction in wear rate).

EXAMPLE 6: PHYSICAL CHARACTERIZATION OF GAMMA-IRRADIATED
UHMWPE WITH OR WITHOUT REMELTING

Materials and Methods

The materials for physical characterization were the same as the wear tested materials described in EXAMPLE 5. The materials included UHMWPE extruded bars (3" in diameter) gamma irradiated to 3.3, 4.5, 9.5, 14.5, 20.2, 24, 50 and 100 Mrad, with or without remelting, and the non-irradiated bars. 8 mm thick disks were cut out of irradiated bars with or without remelting, and sterilized with ethylene oxide. The specimens for DSC and swelling measurements were cut out of the center of the 8 mm thick disks. The DSC measurement for crystallinity and melting temperature with sample weighing about 4 mg was described in EXAMPLE 1. For swelling measurements, 1 mm thick sheet weighing about 0.5 gram was cut out of the center of the 8 mm thick disk, and extraction of the sol-fraction was performed in boiling p-xylene for 72 hours, with 0.5 wt % antioxidant (2,6-di-t-butyl-4-methyl phenol) being added to prevent oxidation. After extraction, the gel was transferred to fresh p-xylene and allowed to equilibrate at 120°C for 2 hours. The swollen gel was then quickly transferred to a weighing bottle, covered and weighed. The data was obtained as the average of five measurements. After measurements, samples were deswollen in acetone and then dried at 60°C in a vacuum oven to a constant weight. The gel fraction was determined as the ratio of the weight of the dried extracted to the initial dry non-extracted network. The degree of swelling was calculated as the ratio of the weight of the swollen gel to the dried extracted gel. The degree of swelling was used to calculate the network chain density, number-average molecular weight between crosslinks and crosslink density, according to the theory of Flory and Rehner {Shen et al., J. Polym. Sci., Polym. Phys., 34:1063-1077 (1996)}. For examining the

oxidation profiles of the extruded bars irradiated and remelted in air, a two hundred micron thick section was microtomed perpendicular to the bar surface and examined by FTIR as a function of depth from the bar surface.

Results and Discussion

The melting temperature and crystallinity for non-irradiated, and irradiated (with and without remelting) materials are shown in Table 6. The degree of swelling, average molecular weight between crosslinks, crosslink density and gel content are shown in Table 7. After irradiation, the melting temperature and crystallinity increased, ranging from 135.3 to 140.2°C, and about 60 to 71%, respectively, over the dose range studied. Remelting of the irradiated bars resulted in reductions in the melting temperature and crystallinity, ranging from about 131 to 135°C, and about 51 to 53%, respectively.

As shown in Table 7, with increasing radiation dose, the degree of swelling and average molecular weight between crosslinks decreased, while the crosslink density increased. The gel content, in general, increased with radiation dose, but reached a plateau region at about 9.5 Mrad. With remelting, the degree of swelling and average molecular weight between crosslinks for bars irradiated up to 9.5 Mrad were significantly reduced, but remained almost unchanged after 9.5 Mrad. The crosslink density increased, after remelting, with dose up to 9.5 Mrad and then remained almost unchanged. The gel content, generally, increased after remelting.

The oxidation profiles for the 9.5 and 24 Mrad materials, after remelting at 150°C in air for 5 hours, as a function of depth from the bar surface are shown in Fig. 24. The results clearly showed that the oxidation drops tremendously within 1 mm, and the most oxidized layer is about 1 mm deep below the surface, after irradiation and remelting in air.

20 EXAMPLE 7: TENSILE PROPERTIES OF GAMMA-IRRADIATED UHMWPE AT
VARIOUS DOSES, WITH OR WITHOUT REMELTING

Materials and Methods

25 The materials for tensile test are the same as the wear
tested materials described in EXAMPLE 5, above. The materi-
als included UHMWPE extruded bars (3" in diameter) gamma
irradiated to 4.5, 9.5, 14.5, 20.2, and 24 Mrad, with or
without remelting, and non-irradiated bars. Five tensile
specimens each was machined out of the center of the 3"
diameter bars according to ASTM F648-96 and D-638 (type IV).
30 Tensile tests were performed using an servo-hydraulic ten-
sile test machine at speed of 2 inches/min.

Results and Discussion

35 The tensile strength at yield, elongation, and tensile
strength (ultimate) at breaks are shown in Table 8. The
average tensile properties as a function of radiation dose
are shown in Figs. 25-27. The tensile strength at yield
after irradiation was higher than that of non-irradiated
material, and slightly increased with radiation dose.
40 Remelting of the irradiated bars resulted in a reduction in
tensile strength at yield, and the strength remained almost
constant over the dose range studied (Fig. 25). The tensile
strength (ultimate) and elongation at break decreased with
increasing doses (Figs. 26-27). Remelting resulted in
45 further reduction in ultimate tensile strength over the dose
range. However, remelting had almost no effect on the
elongation at break over the same dose range.

50 All publications and patent applications mentioned in
this Specification are herein incorporated by reference to
the same extent as if each of them had been individually
indicated to be incorporated by reference.

20 Although the foregoing invention has been described in
some detail by way of illustration and example for purposes
of clarity and understanding, it will be obvious that vari-
ous modifications and changes which are within the skill of
those skilled in the art are considered to fall within the
scope of the appended claims. Future technological advance-
25 ments which allows for obvious changes in the basic inven-
tion herein are also within the claims.

Table 1 3.3 Mrad

Distance from surface (mm)	Before remelting			After remelting		
	peak melting temperature (°C)	degree of crystallinity (%)	gel content (%)	peak melting temperature (°C)	degree of crystallinity (%)	gel content (%)
34.8 - 35	135.3	59.6	91	131.4	52.5	94.7
35.8 - 36	135.4	60.2	91	131.5	51.2	94.7
36.8 - 37	135.3	60.5	91	131.4	51.9	94.7
37.8 - 38 (center)	135.3	60	91.1	131.3	52	95

Table 2 28 Mrad

Distance from surface (mm)	Before remelting			After remelting		
	peak melting temperature (°C)	degree of crystallinity (%)	gel content (%)	peak melting temperature (°C)	degree of crystallinity (%)	gel content (%)
34.8 - 35	139.8	65.1	95.8	135	52	97.7
35.8 - 36	139.8	64.2	95.8	134.8	52.1	97.7
36.8 - 37	139.7	64.5	95.8	134.9	52.5	97.7
37.8 - 38 (center)	139.7	65.3	95.8	134.9	52.7	97.7

Table 3

Cup #	Material	Wear Rate (mm ³ /million cycles)	Mean Wear Rate \pm Std Deviation
N11	3.3 Mrad Not remelted	20.8	21.1 \pm 0.3
N16		21.2	
N17		21.4	
R21	3.3 Mrad Remelted	17.7	18.6 \pm 1.3
R26		20.1	
R27		18.0	
N35	28 Mrad Not remelted	0.29	0.25 \pm 0.03
N31		0.24	
N32		0.24	
R48	28 Mrad Remelted	0.36	0.36 \pm 0.001
R45		0.35	
R49		0.36	

Table 4

Cup #	Material	0 - 3 Million Cycles (non- aged)		3 - 7 Million Cycles		
		Wear Rate (mm ³ /million cycles)	Mean Wear Rate \pm Std Deviation	Conditions	Wear Rate (mm ³ /million cycles)	Mean Wear Rate \pm Std Deviation
N11	3.3 Mrad Not remelted	20.8	21.1 \pm 0.3	non-aged	21.2	-
N16		21.2		aged	21.5	21.8 \pm 0.5
N17		21.4		aged	22.2	
R21	3.3 Mrad Remelted	17.7	18.6 \pm 1.3	non-aged	17.5	-
R26		20.1		aged	19.2	19.8 \pm 1.0
R27		18.0		aged	20.5	
N35	28 Mrad Not remelted	0.29	0.25 \pm 0.03	non-aged	0.03	-
N31		0.24		aged	- 0.47	- 0.71 \pm 0.3
N32		0.24		aged	- 0.93	
R48	28 Mrad Remelted	0.36	0.36 \pm 0.001	non-aged	0.47	-
R45		0.35		aged	0.08	- 0.06 \pm 0.2
R49		0.36		aged	- 0.20	

Table 5 (1 - 5 million cycles)

Cup #	Material	Wear Rate (mm ³ /million cycles)	Mean Wear Rate \pm SD (mm ³ /million cycles)
N11	3.3 Mrad Not remelted	20.46	20.12 \pm 0.7 *
N16		19.32	
N17		20.59	
R21	3.3 Mrad Remelted	17.04	17.51 \pm 0.48 *
R26		18.0	
R27		17.49	
RA2	4.5 Mrad Remelted	9.93	9.28 \pm 0.92
RA3		8.63	
RB3	9.5 Mrad Remelted	2.39	2.22 \pm 0.24
RB6		2.05	
RC5	14.5 Mrad Remelted	1.26	1.17 \pm 0.13
RC6		1.08	
RD1	20.2 Mrad Remelted	0.26	0.12 \pm 0.2
RD6		-0.02	
RE3	24 Mrad Remelted	-0.49	-0.59 \pm 0.13
RE4		-0.68	
RF2	50 Mrad Remelted	-0.8	—
RG1	100 Mrad Remelted	-6.88**	—

*The wear data of the 3.3 Mrad materials in Example 2.

**The wear rate in the period of 1 - 2 million cycles.

Table 6

Samples	Non-remelted		Remelted	
	Melting point (°C)	Crystallinity (%)	Melting point (°C)	Crystallinity (%)
Non-irrad.	133.8	55	-	-
3.3 Mrad	135.3 ± 0.1	60.1 ± 0.4	131.4 ± 0.1	51.8 ± 0.6
4.5 Mrad	136.2 ± 0.2	65.8 ± 1.6	131.6 ± 0.2	52.0 ± 1.3
9.5 Mrad	137.1 ± 0	67.1 ± 2.2	134.8 ± 0.2	53.3 ± 2.1
14.5 Mrad	137.5 ± 0.2	69.6 ± 1.6	135.0 ± 0.1	53.0 ± 1.5
20.2 Mrad	137.4 ± 0.1	70.8 ± 2.8	135.3 ± 0.1	52.1 ± 1.8
24 Mrad	137.9 ± 0.3	68.0 ± 1.3	135.2 ± 0.1	51.7 ± 1.2
50 Mrad	138.9 ± 0.2	67.0 ± 1.3	135.2 ± 0	52.8 ± 0.2
100 Mrad	140.2 ± 0.3	66.3 ± 2.7	130.8 ± 0.2	52.3 ± 1.7

Table 7

Samples	Non- remelted				Remelted			
	Degree of swelling	M.W. between crosslinks (g/mol)	Crosslink density (mol%)	Gel content (%)	Degree of swelling	M.W. between crosslinks (g/mol)	Crosslink density (mol%)	Gel content (%)
3.3 Mrad	5.29	8400	0.17	94.7	3.21	2500	0.56	98.1
4.5 Mrad	3.57	3500	0.40	97.8	3.15	2400	0.58	98.4
9.5 Mrad	2.82	1900	0.74	98.6	2.54	1400	1.0	98.9
14.5 Mrad	2.35	1100	1.27	98.7	2.36	1100	1.27	99.2
20.2 Mrad	2.27	1000	1.40	98.8	2.25	1000	1.40	99.2
24 Mrad	2.17	900	1.56	98.7	2.24	1000	1.40	99.2
50 Mrad	1.92	600	2.33	98.7	2.17	900	1.56	99.1
100 Mrad	1.71	400	3.50	98.6	1.71	400	3.50	98.5

Table 8

Materials	Tensile Strength at Yield (MPa)	Tensile Strength at Break (MPa)	Elongation at Break (%)
Non-irradiated	23.3 ± 0.11	52.1 ± 4.78	356 ± 23
Without remelting			
4.5 Mrad	24.9 ± 0.33	46.9 ± 2.91	314 ± 12
9.5 Mrad	25.3 ± 0.12	47.6 ± 2.76	251 ± 8
14.5 Mrad	25.7 ± 0.25	46.4 ± 1.20	213 ± 5
20.2 Mrad	26.2 ± 0.27	40.2 ± 2.72	175 ± 7
24 Mrad	26.4 ± 0.23	40.0 ± 5.42	164 ± 17
After remelting			
4.5 Mrad	21.5 ± 0.33	45.6 ± 8.89	309 ± 20
9.5 Mrad	21.3 ± 0.60	43.2 ± 2.80	252 ± 8
14.5 Mrad	21.8 ± 0.29	36.8 ± 1.72	206 ± 9
20.2 Mrad	21.9 ± 0.18	34.3 ± 3.61	185 ± 8
24 Mrad	21.7 ± 0.25	32.3 ± 2.81	160 ± 19

We claim:

20

1. A preformed polymeric composition comprising a crosslinked thermally treated polymer.

25

2. The composition of claim 1, wherein the composition possesses one or more of the following characteristics: degree of swelling of between about 1.7 to about 5.3; molecular weight between crosslinks of between about 400 to about 8400 g/mol; and a gel content of between about 95 to about 99 %.

30

3. The composition of claim 1, wherein the preformed polymeric composition is crosslinked by gamma radiation at a dose from about 1 to about 100 Mrad.

35

4. The composition of claim 3, wherein the dose is from about 5 to about 25 Mrad.

40

5. An in vivo implant comprising a crosslinked and remelted polymer.

45

6. A method for increasing the wear resistance of a preformed polymeric composition, comprising the steps of:
(a) crosslinking the polymeric composition in a solid state; and
(b) subjecting the crosslinked polymeric composition to thermal treatment.

50

7. The method of claim 6, further comprising the step of removing the most oxidized surface of the thermally treated crosslinked polymeric composition.

8. The method of claim 6, wherein the crosslinking is by gamma irradiation.

20 9. The method of claim 8, wherein the gamma irradiation is at a dose of from about 1 to about 100 Mrad.

10. The method of claim 6, wherein the thermal treatment comprises remelting the crosslinked polymer.

25 11. The method of claim 10, wherein the remelting temperature is between the melting temperature of the irradiated polymer to about 160°C above the melting temperature of the irradiated polymer.

30 12. The method of claim 6, wherein the resulting polymeric composition possesses one or more of the following characteristics: degree of swelling of between about 1.7 to about 5.3; molecular weight between crosslinks of between about 400 to about 8400 g/mol; and a gel content of between
35 about 95 to about 99 %.

13. The method of claim 6, wherein the thermal treatment comprises annealing the crosslinked polymer.

40 14. The method of claim 13, wherein the annealing temperature is from about 90°C below to about 1°C below the melting temperature of the irradiated polymer.

45 15. A polymeric composition made from the steps of:
(a) crosslinking a starting polymer in a solid state to form a crosslinked polymer; and
(b) subjecting the crosslinked polymer to thermal treatment.

50 16. The polymeric composition of claim 15, further comprising the step of removing the most oxidized surface of the crosslinked polymeric composition.

20 17. The polymeric composition of claim 15, wherein the crosslinking is by gamma irradiation.

25 18. The polymeric composition of claim 17, wherein the gamma irradiation is at a dose of from about 1 to about 100 Mrad.

19. The polymeric composition of claim 15, wherein the thermal treatment comprises remelting the crosslinked polymer.

30 20. The polymeric composition of claim 19, wherein the remelting temperature is between the melting temperature of the irradiated polymer to about 160°C above the melting temperature of the irradiated polymer.

35 21. The polymeric composition of claim 15, wherein the thermal treatment comprises annealing the crosslinked polymer.

40 22. The method of claim 21, wherein the annealing temperature is between about 90°C below to about 1°C below the melting temperature of the irradiated polymer.

23. A product made by the process of:
45 (a) crosslinking a preformed polymeric composition in a solid state;
(b) subjecting the crosslinked polymeric composition to thermal treatment; and
(c) fashioning the product from the crosslinked polymeric composition.

50 24. The product of claim 23, further comprising the step of removing the most oxidized surface of the crosslinked polymer.

20 25. The product of claim 24, wherein the product is an
in vivo implant.

25 26. A method for determining an optimal radiation dose
and thermal treatment for treating a polymer to increase its
wear resistance, when made into a desired product, while
maintaining its desirable physical and/or chemical proper-
ties, the method comprises the steps of:

- 30 (a) irradiating the polymer in the solid state over a
range of radiation doses likely to produce the desirable
wear resistance and physical and/or chemical properties;
- 35 (b) remelting the polymer;
- (c) correlating the radiation doses with the wear rate
of the desired product made from the irradiated remelted
polymer using actual or simulated wear conditions for the
desired product;
- (d) correlating the radiation doses with each of the
physical and/or chemical properties of the desired product
made from the irradiated remelted polymer using actual or
simulated wear conditions for the desired product;
- 40 (e) comparing the correlations in steps (c) and (d) to
determine the optimal radiation dose which will produce a
desirable wear rate while maintaining the desirable physical
and/or chemical properties, if such a radiation dose is
arrived at, use this optimal radiation dose for future
treatment of the polymer;
- 45 (f) if the optimal radiation dose cannot be arrived at
in step (e), then determining a dose that would produce a
desirable wear rate based on the correlation of step (c) and
annealing instead of remelting the polymer which has been
irradiated to said dose;
- 50 (g) correlating the physical and/or chemical proper-
ties of the desired product made from the irradiated and
annealed polymer, using actual or simulated wear conditions

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20 for the desired product, with different annealing times and temperatures;

(h) determining an annealing temperature and time which will provide the desirable wear rate and physical and/or chemical properties, if this is possible, then use the radiation dose and annealing conditions determined at this step for future treatment of the polymer;

25 (i) if step (h) does not provide the desirable wear rate and physical and/or chemical properties, then apply a lower radiation dose and repeat steps (c) to (i) or (h) until the optimal radiation dose and annealing conditions are determined or the steps confirm that no optimal radiation dose and annealing conditions can be obtained for the
30 desired wear rate and physical and/or chemical properties.

27. The method of claim 26, wherein the irradiation is gamma irradiation between a range of about 1 to 100 Mrad;
35 the remelting temperature is between the melting temperature of the irradiated polymer to about 160°C above the melting temperature of the irradiated polymer; and the annealing temperature is between about 90°C below to about 1°C below
40 the melting temperature of the irradiated polymer.

28. A polymer produced by irradiation and thermal treatment, wherein the radiation dose and remelting or annealing conditions are determinable by the method of claim
45 27.

29. An in vivo implant made from the polymer of claim 26, wherein the most oxidized surface of the polymer is removed.

50 30. A process for treating a polymer, wherein the process employs radiation dose and remelting or annealing conditions determinable by the steps of claim 26.

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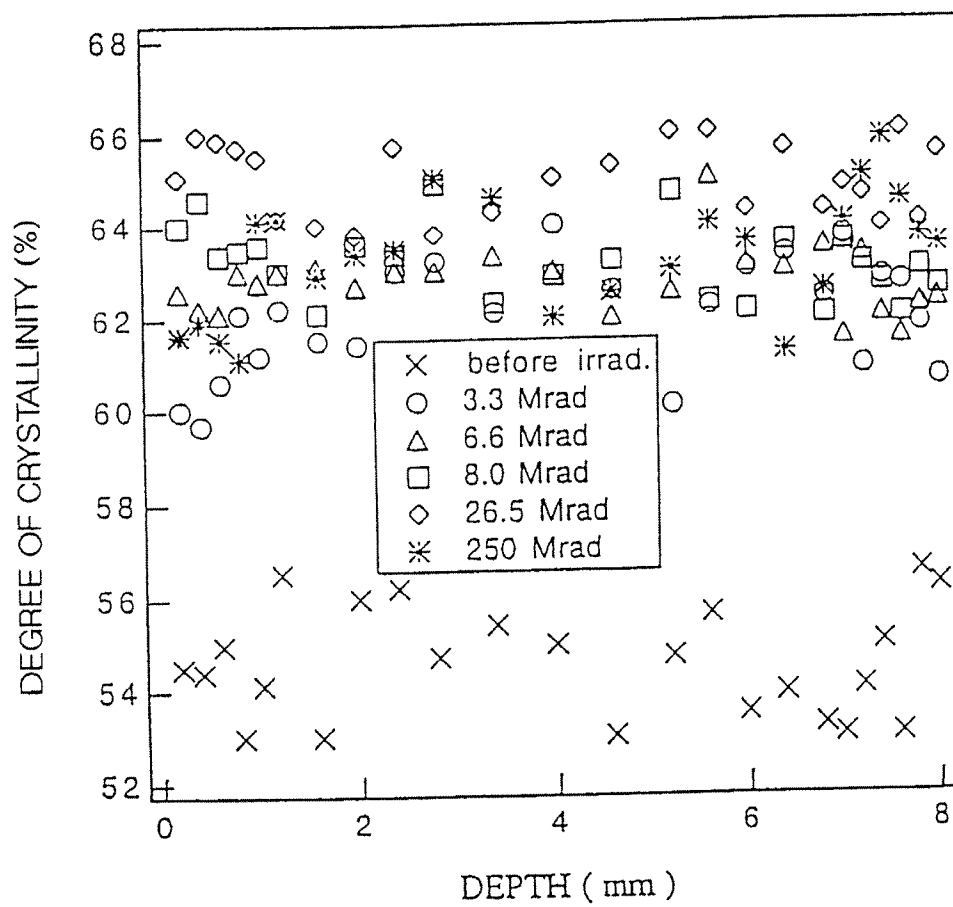


FIG. 1

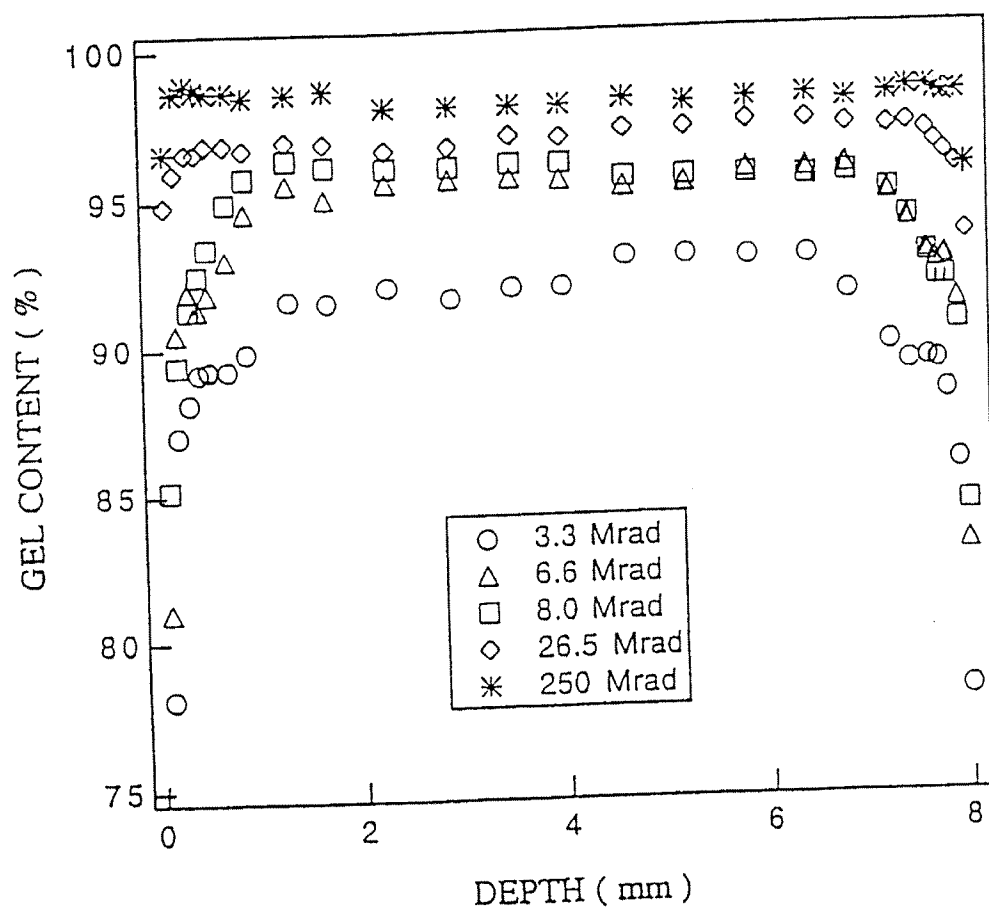
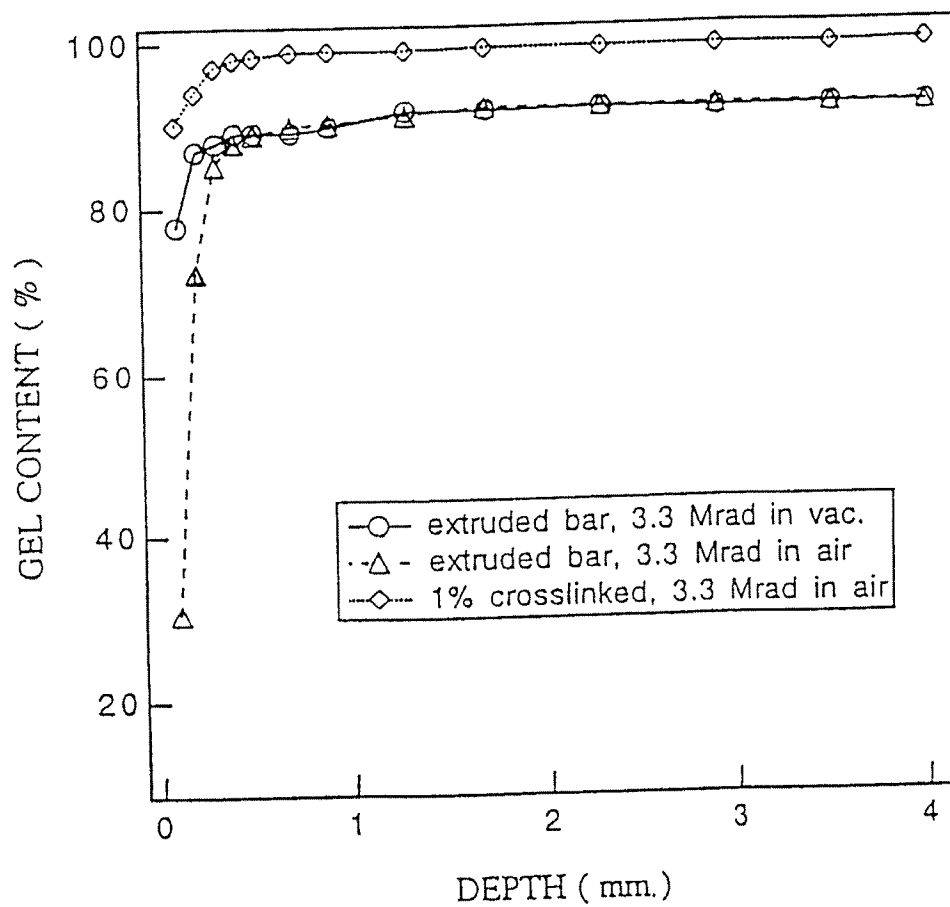


FIG. 2

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**FIG. 3**

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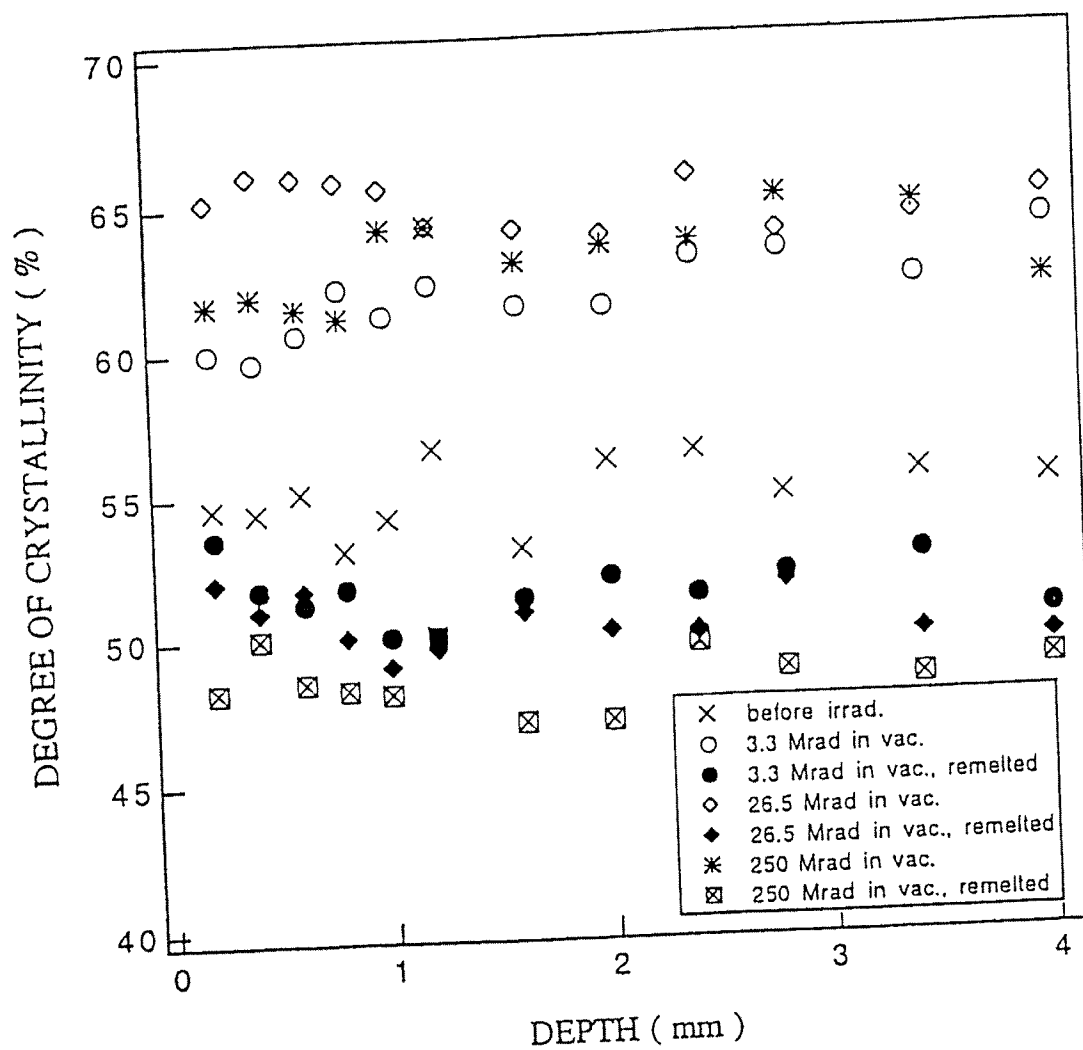


FIG. 4

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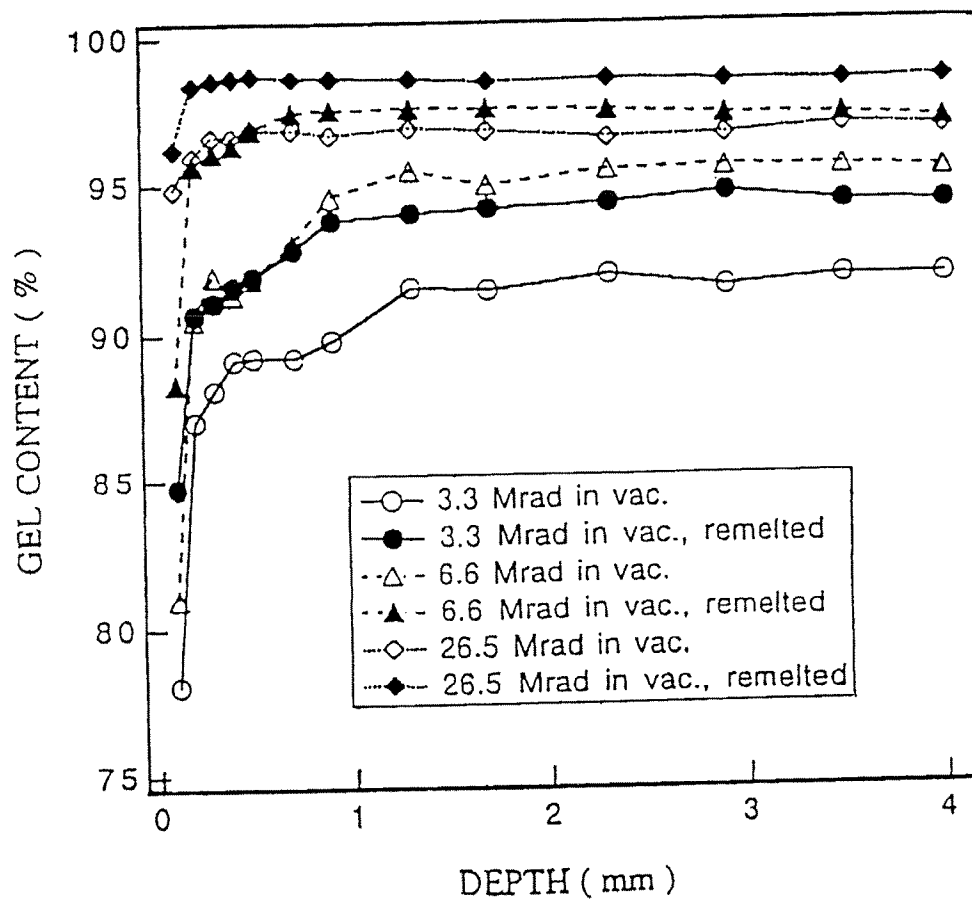
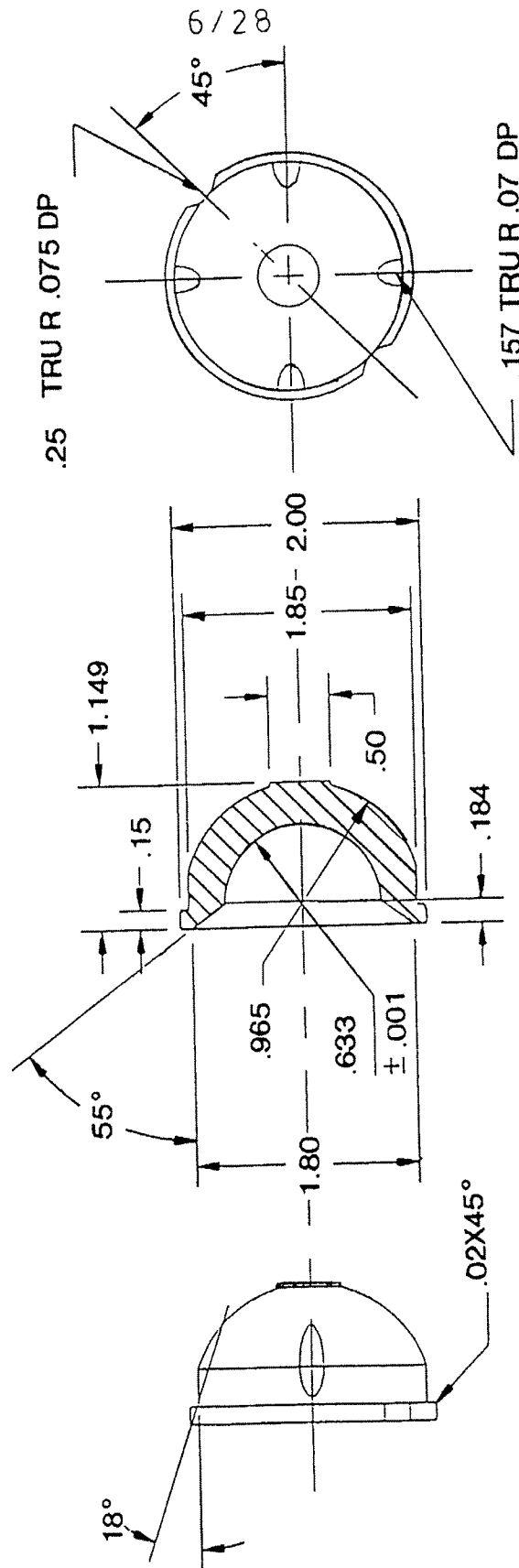


FIG. 5

FIG. 6



CHAMFER .01X45° ALL OTHER PLACES

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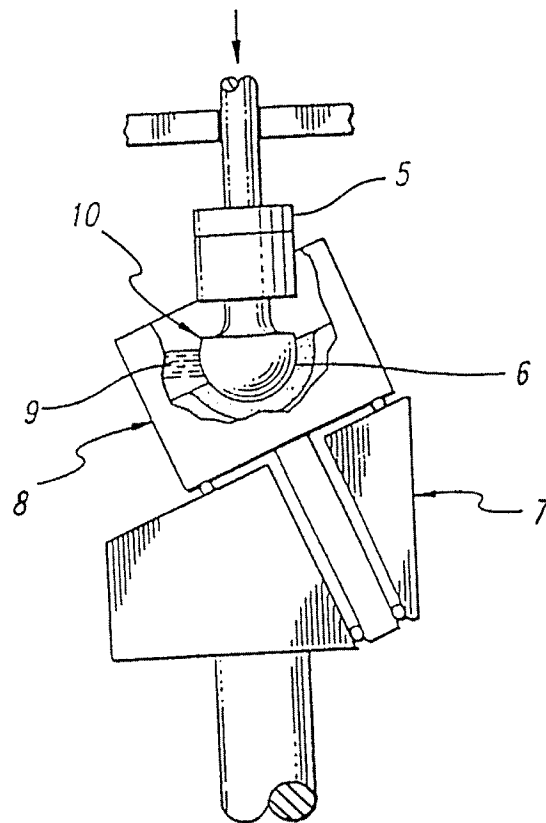


FIG. 7

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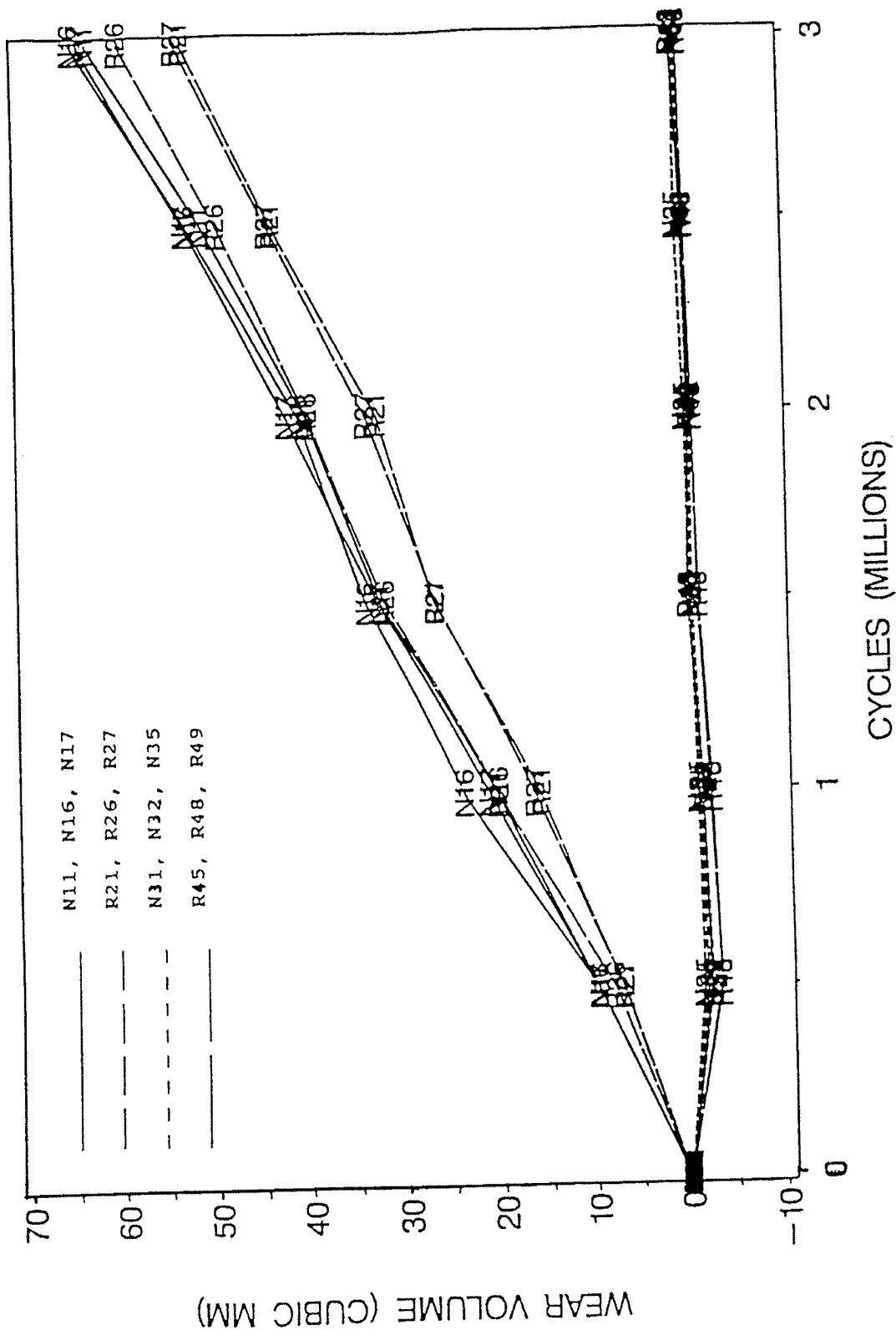


FIG. 8

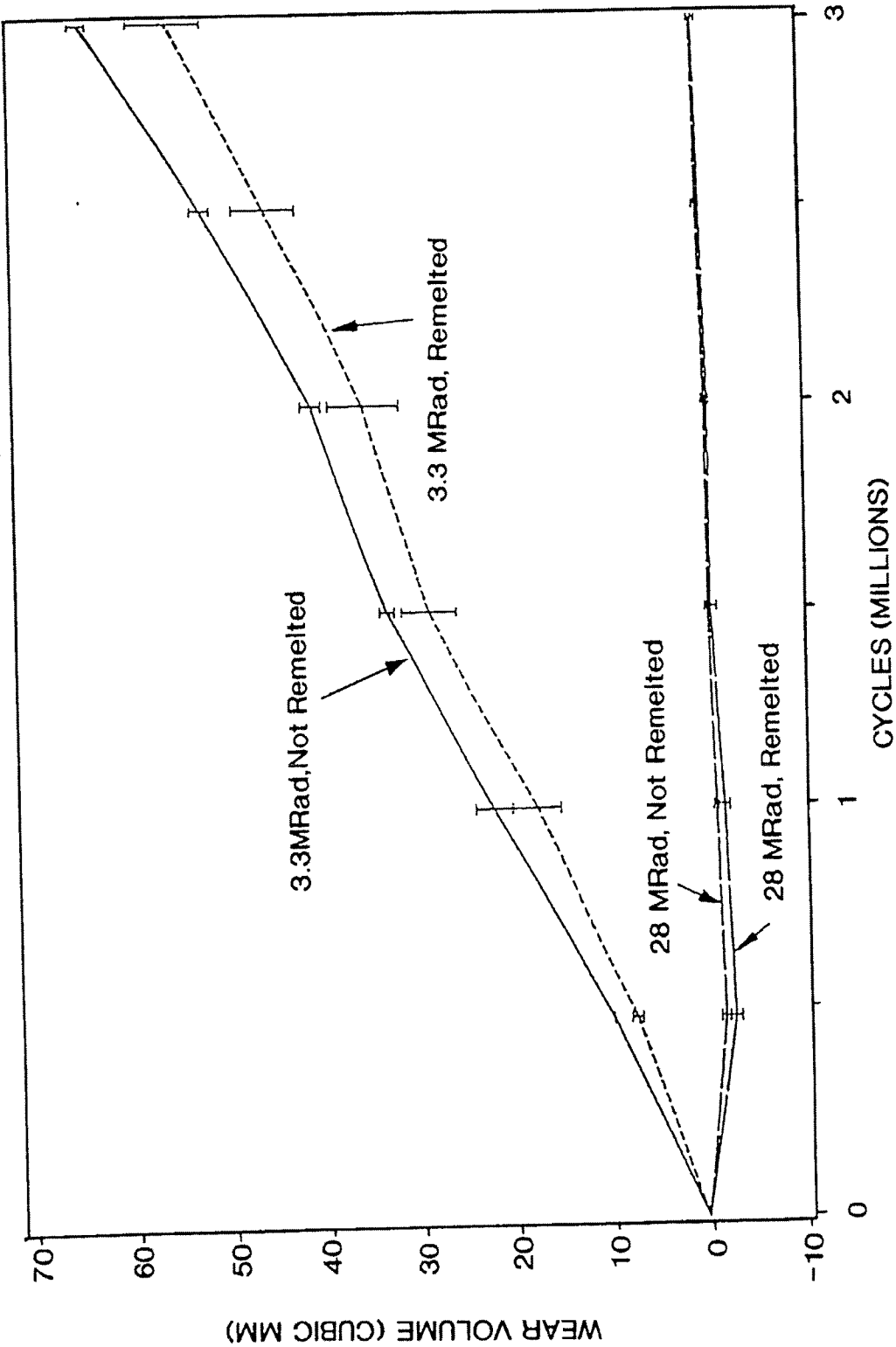


FIG. 9

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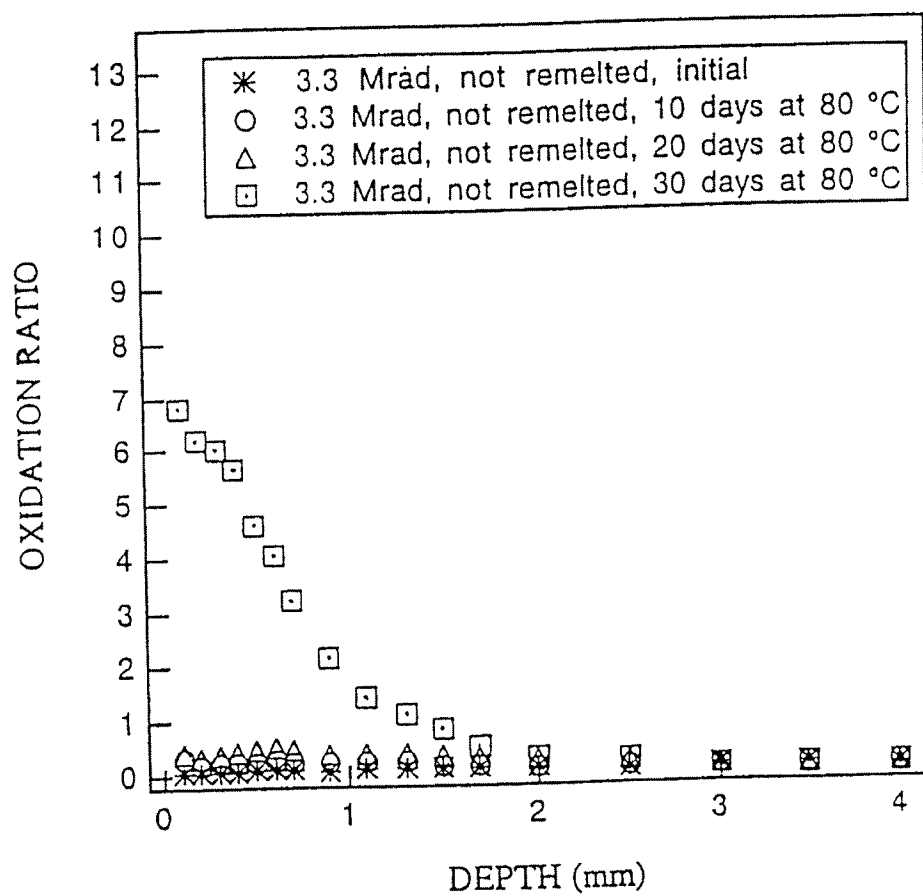


FIG. 10

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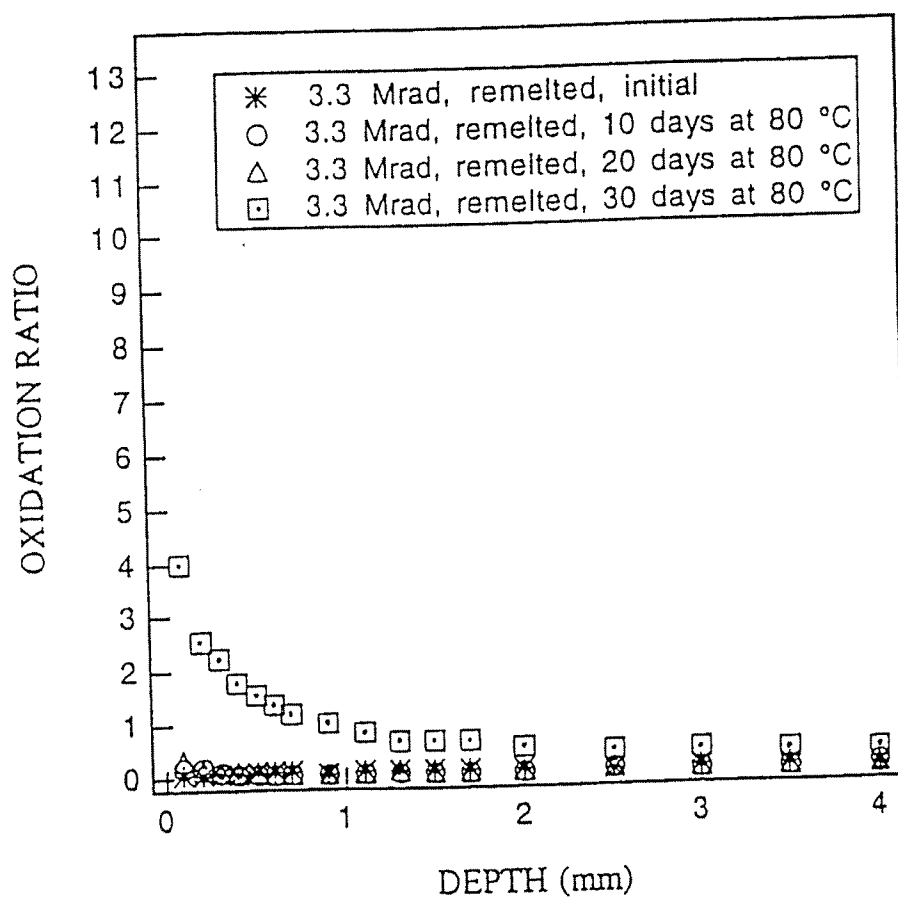


FIG. 11

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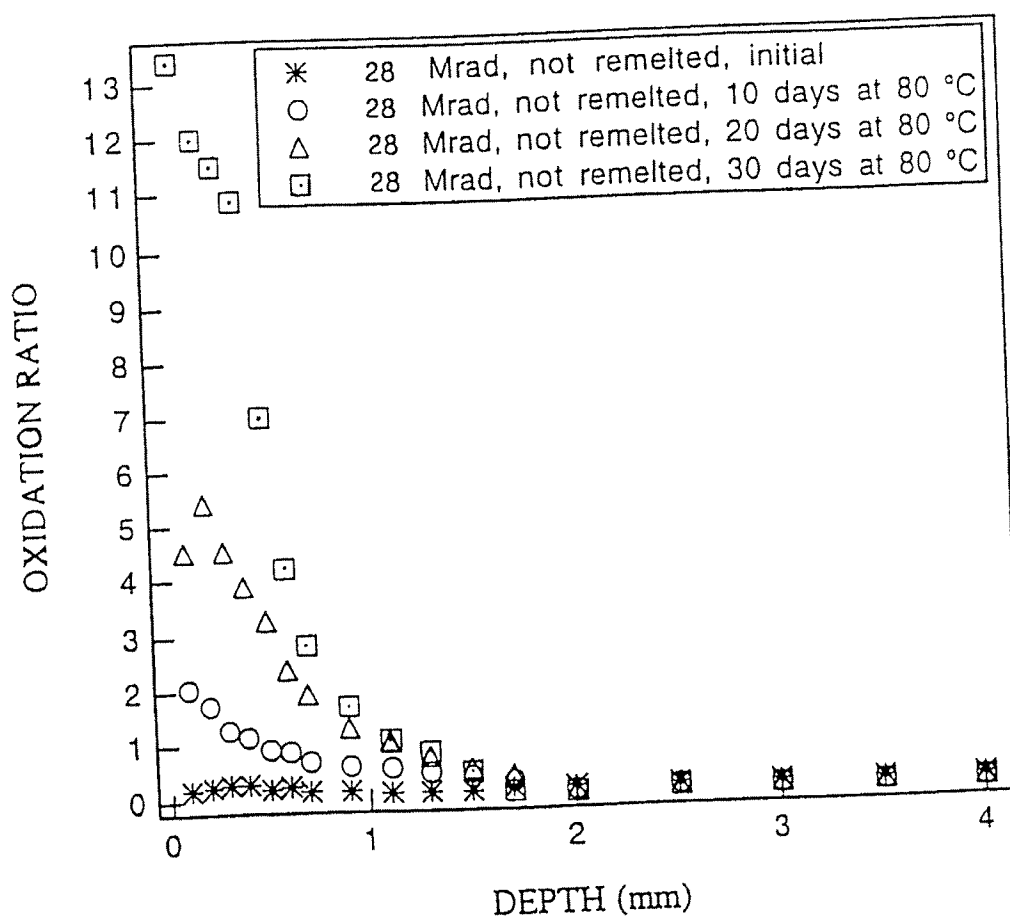


FIG. 12

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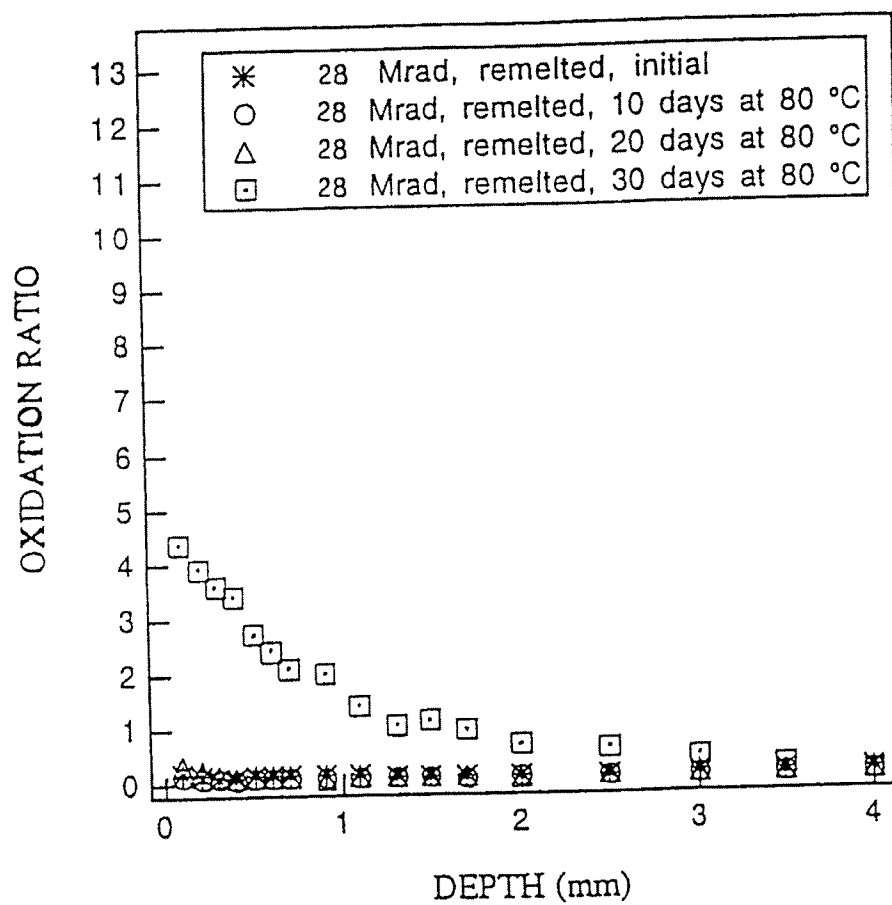


FIG. 13

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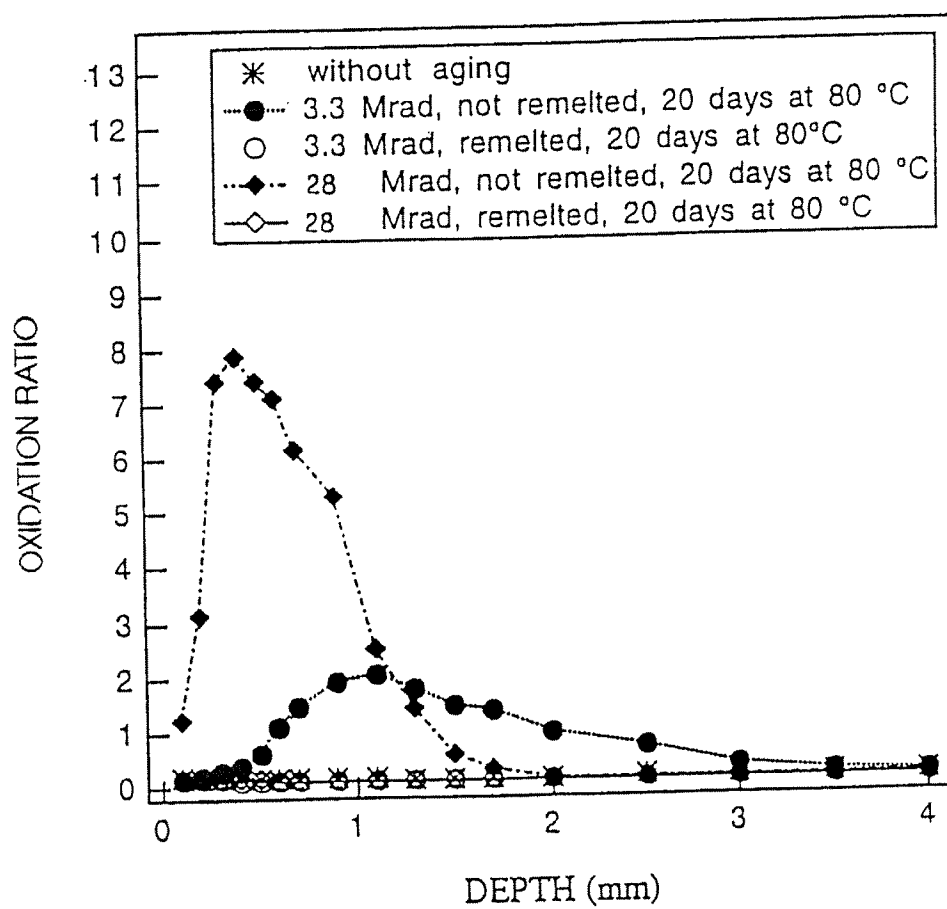


FIG. 14

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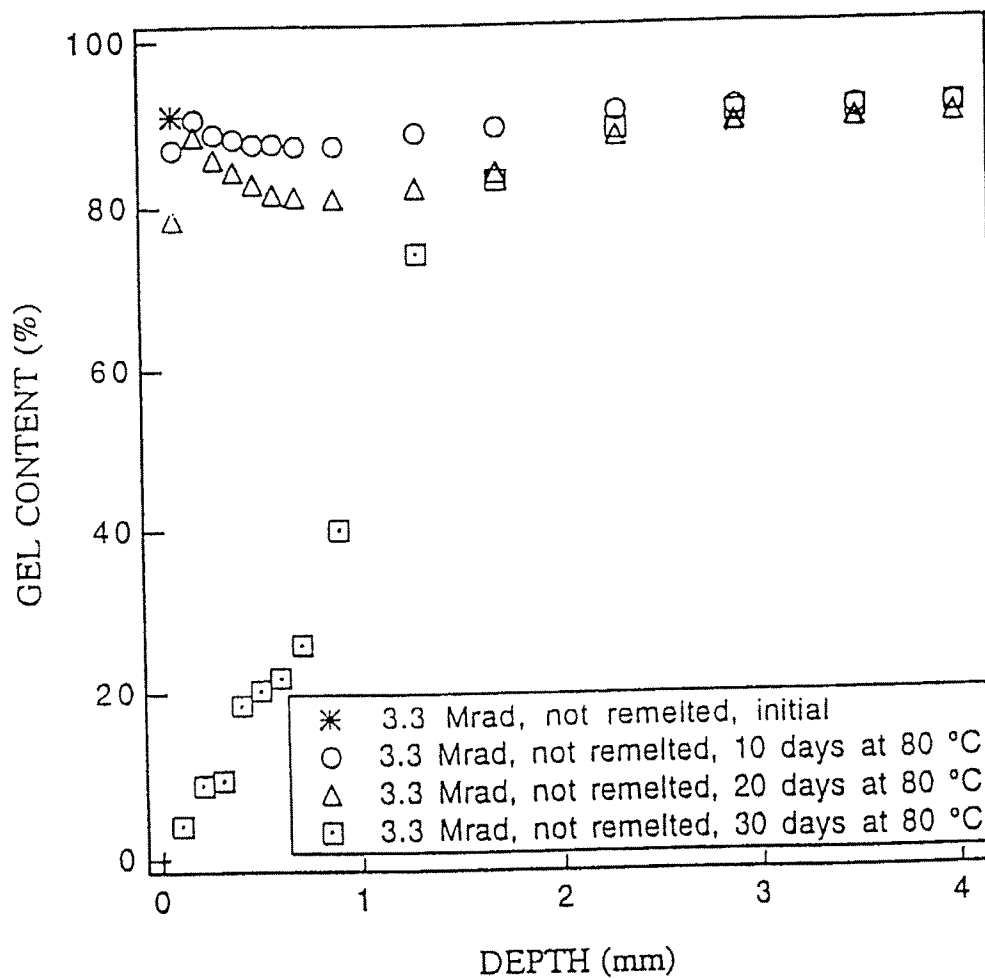


FIG. 15

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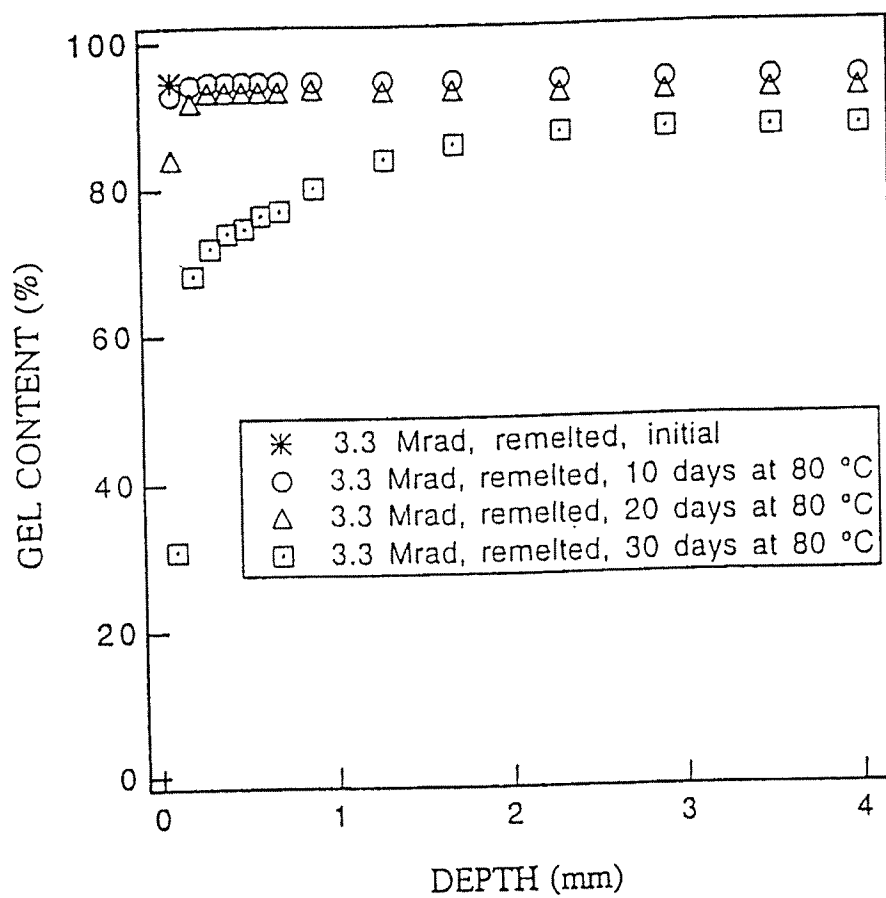


FIG. 16

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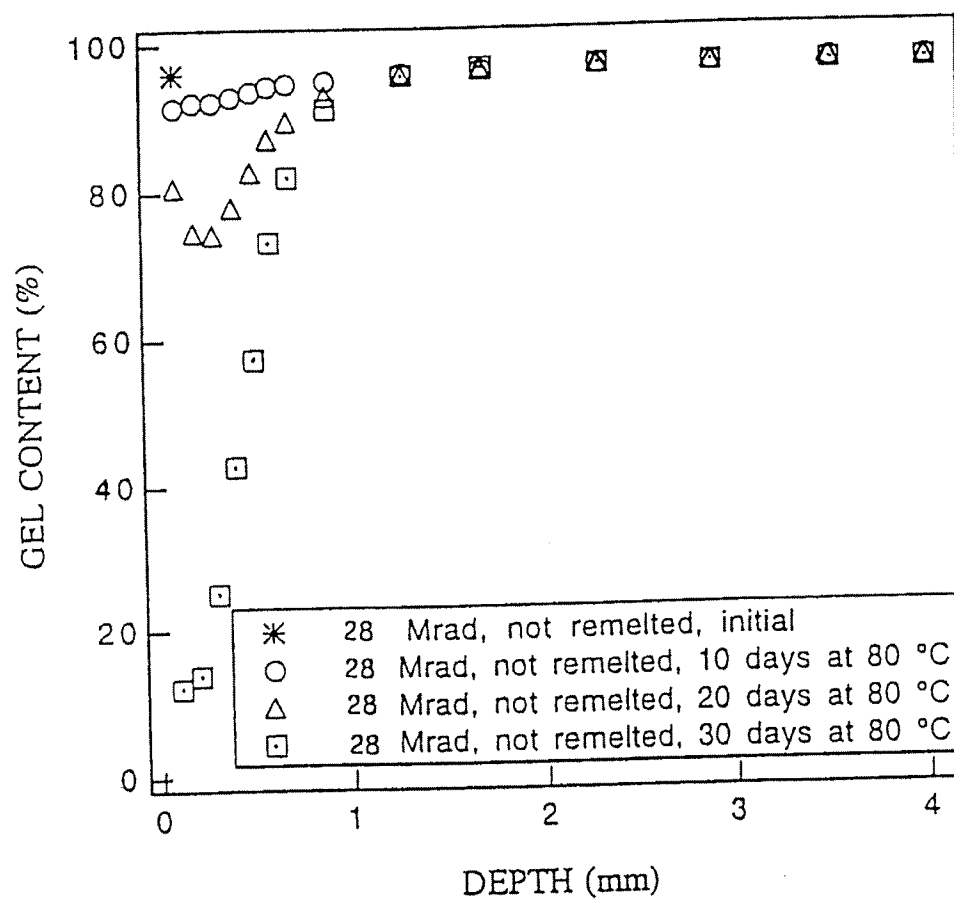


FIG. 17

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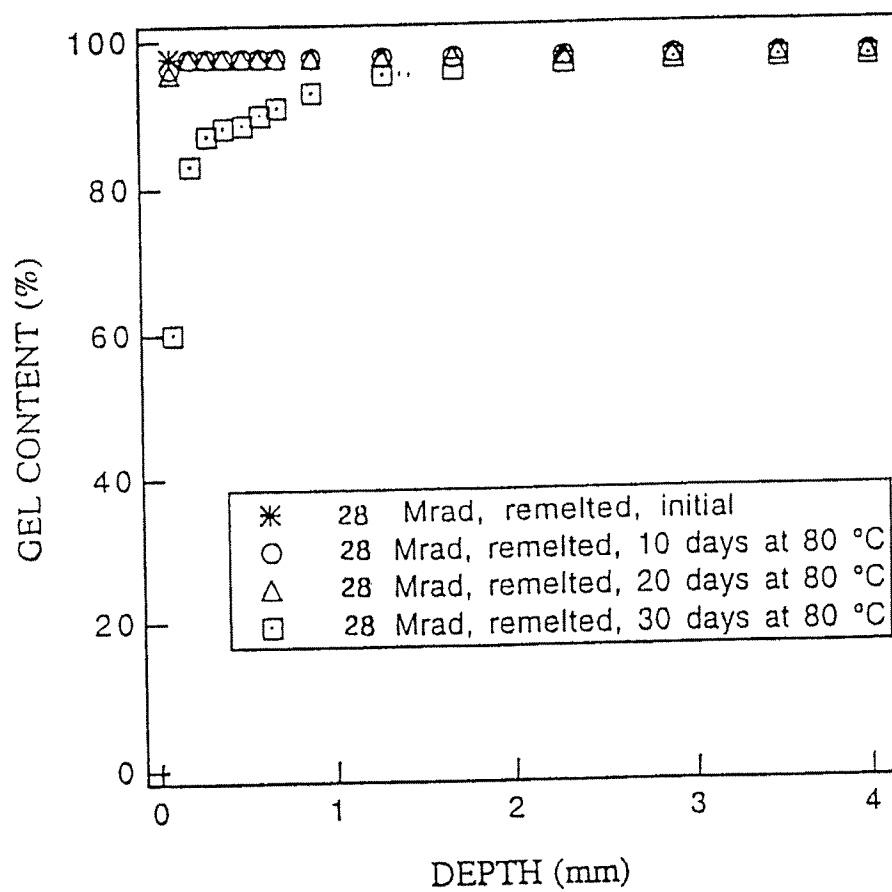


FIG. 18

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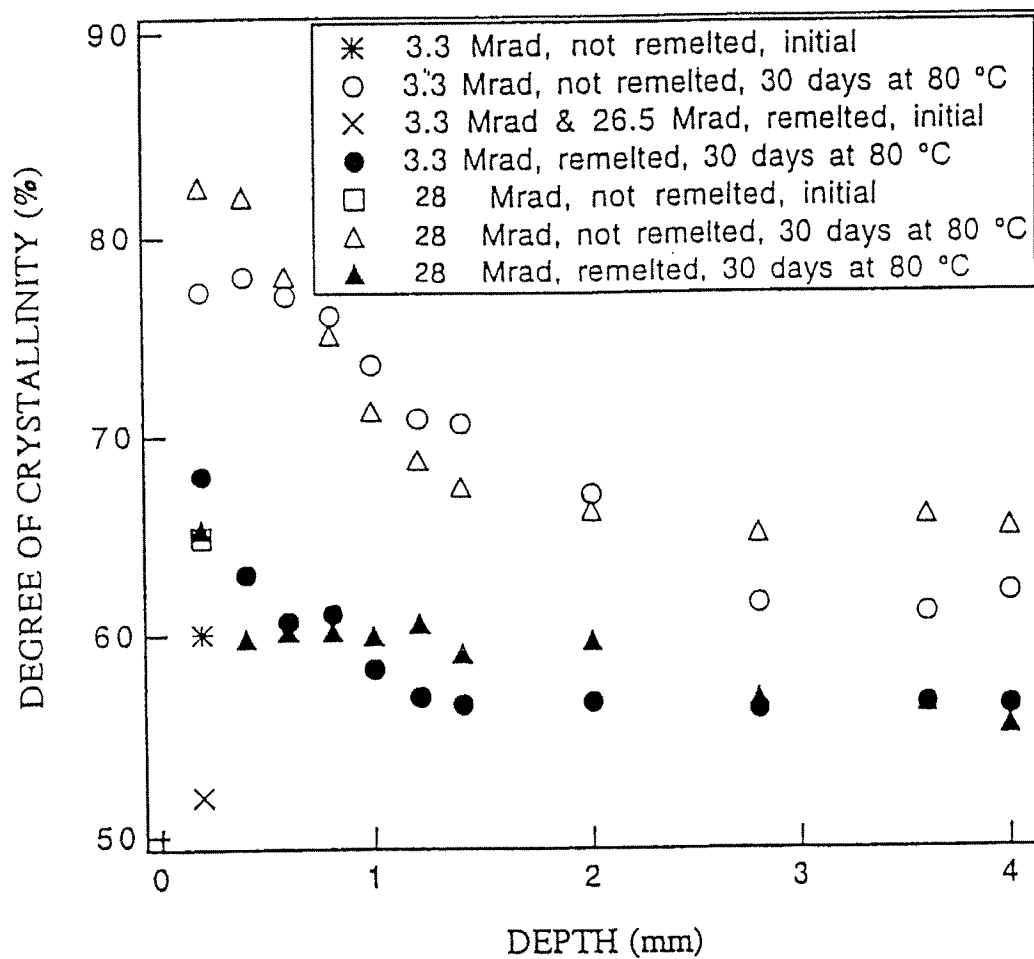


FIG. 19

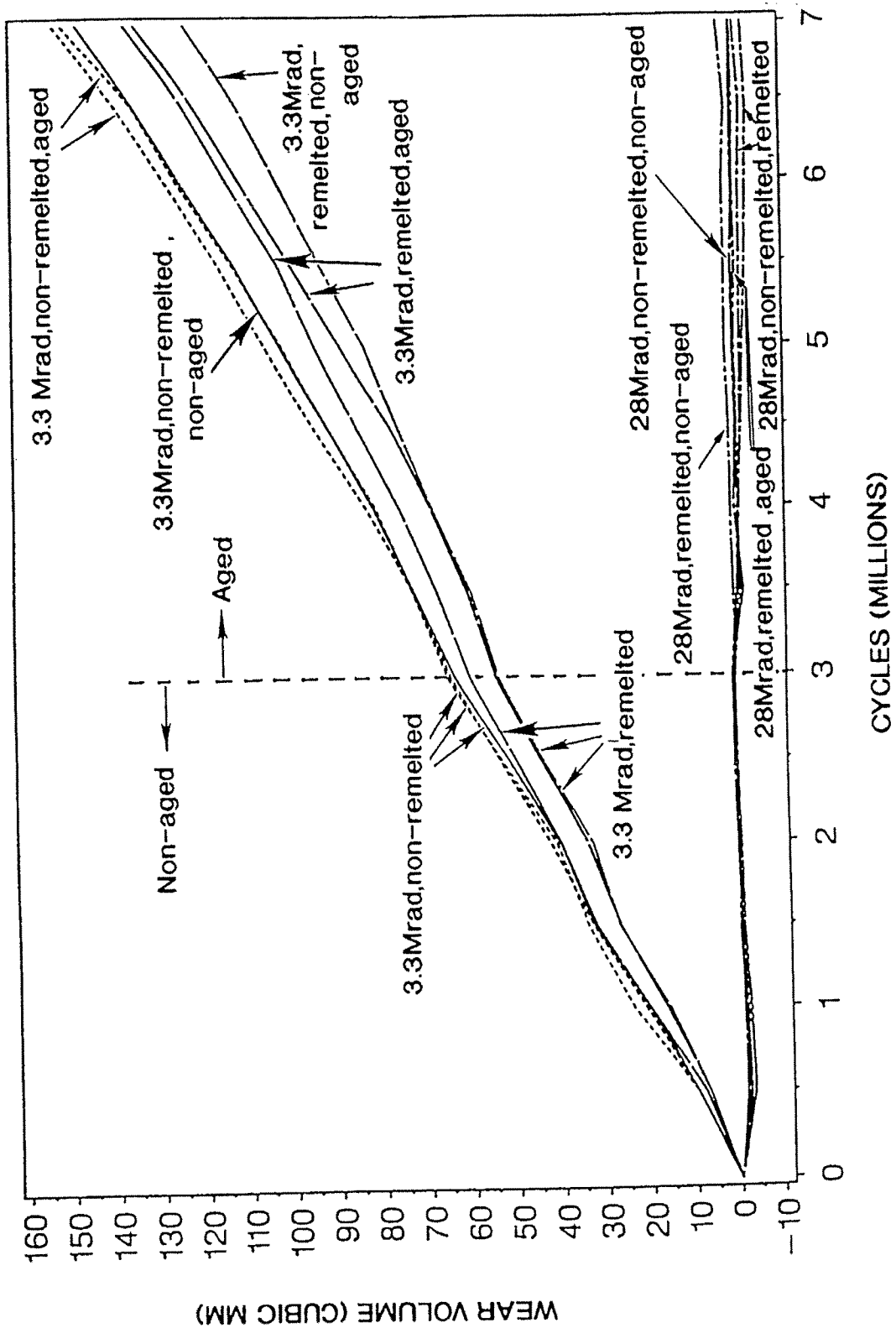


FIG. 20

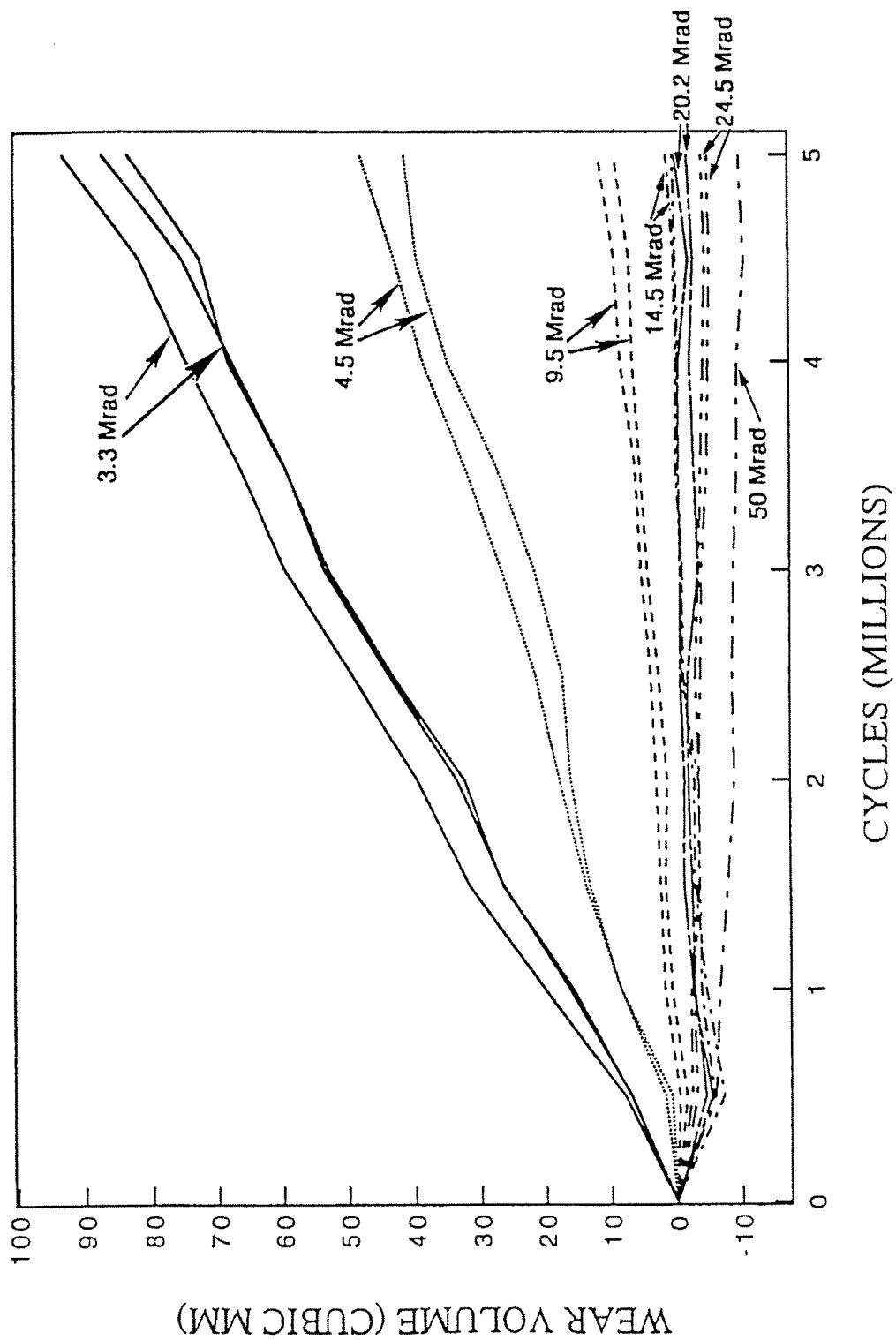


FIG. 21

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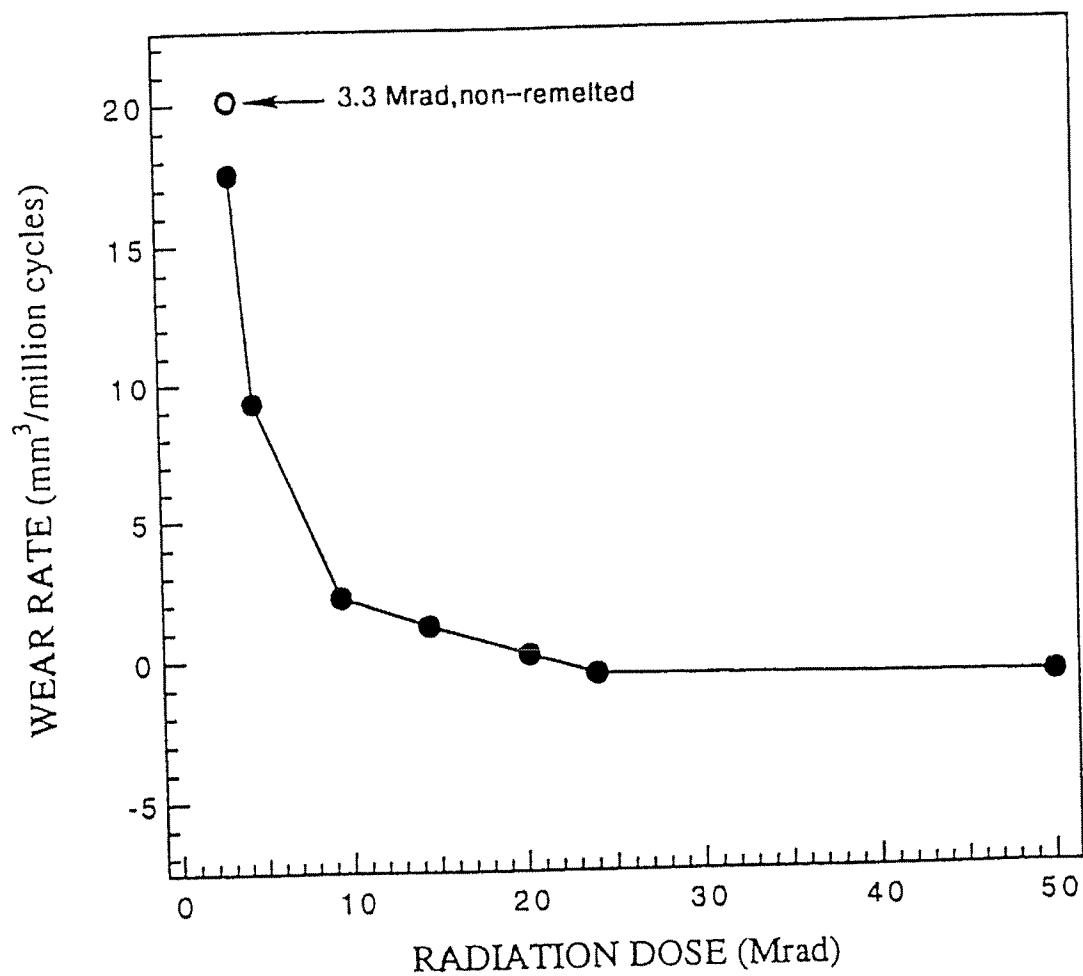


FIG. 22

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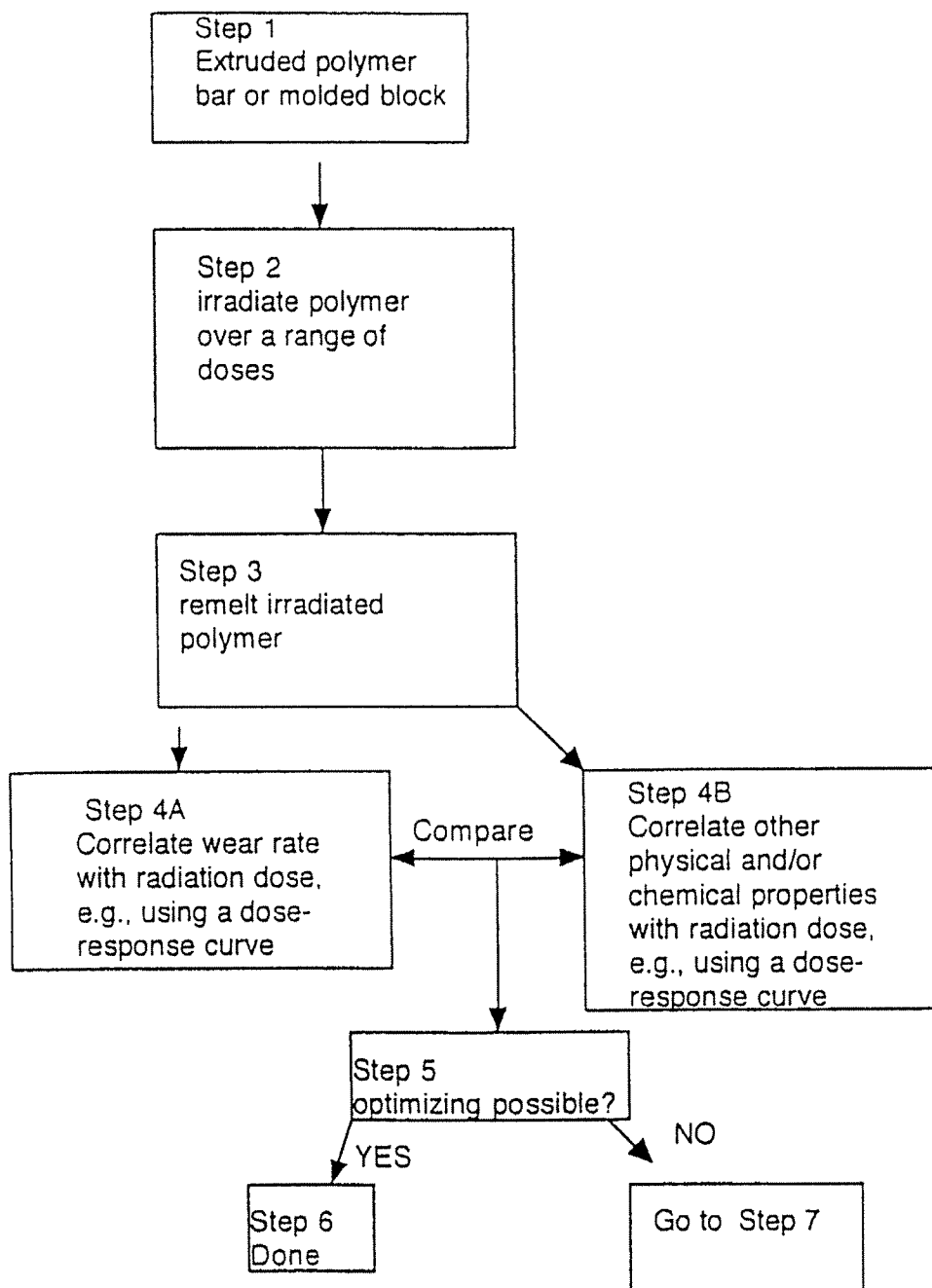


FIG. 23A

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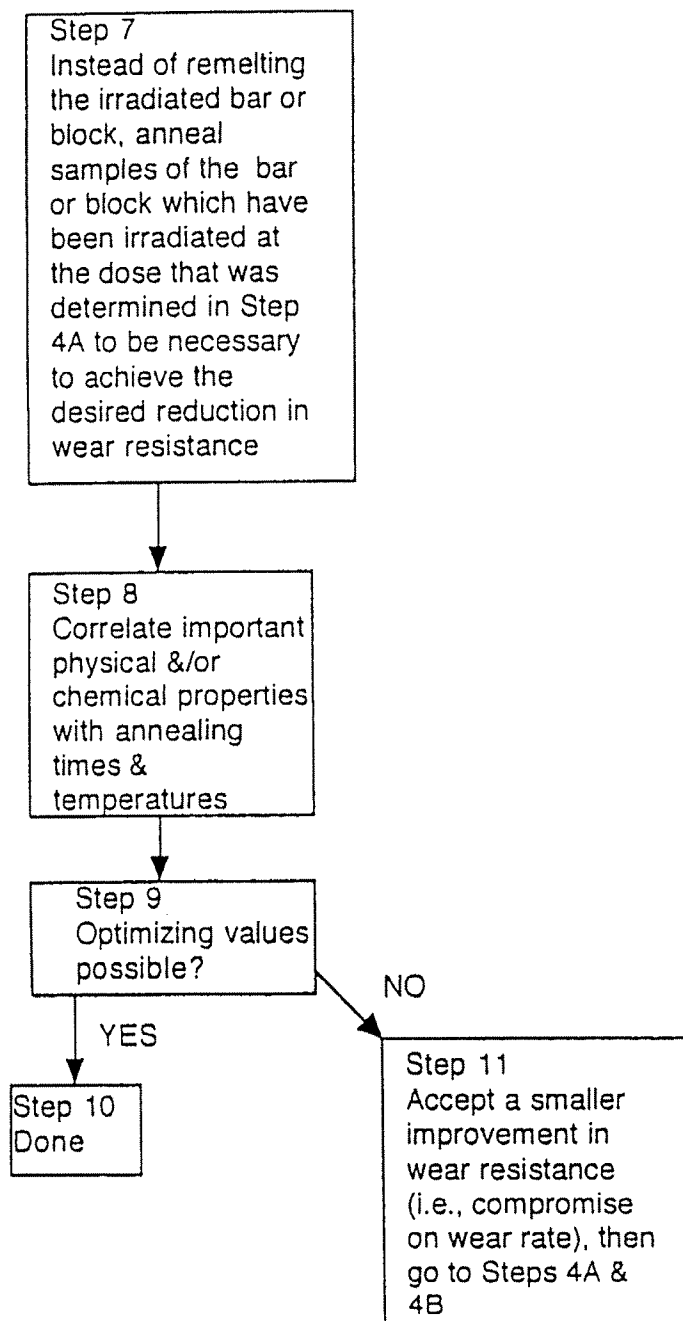


FIG. 23B

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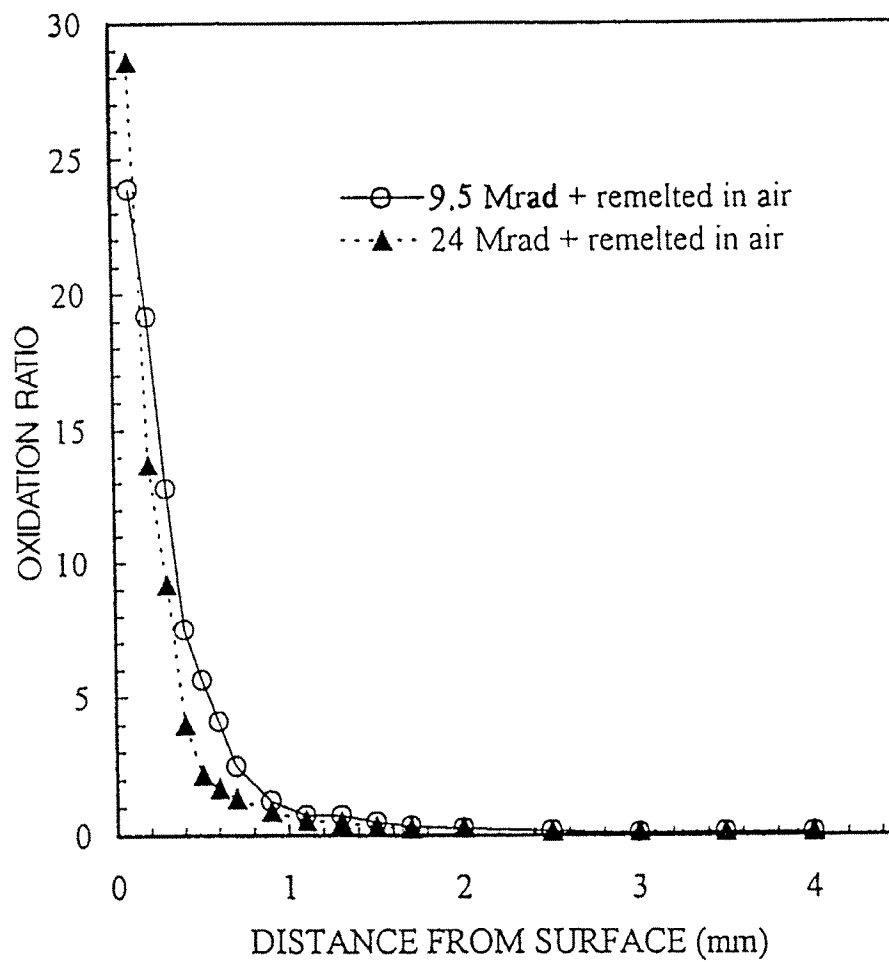


FIG. 24

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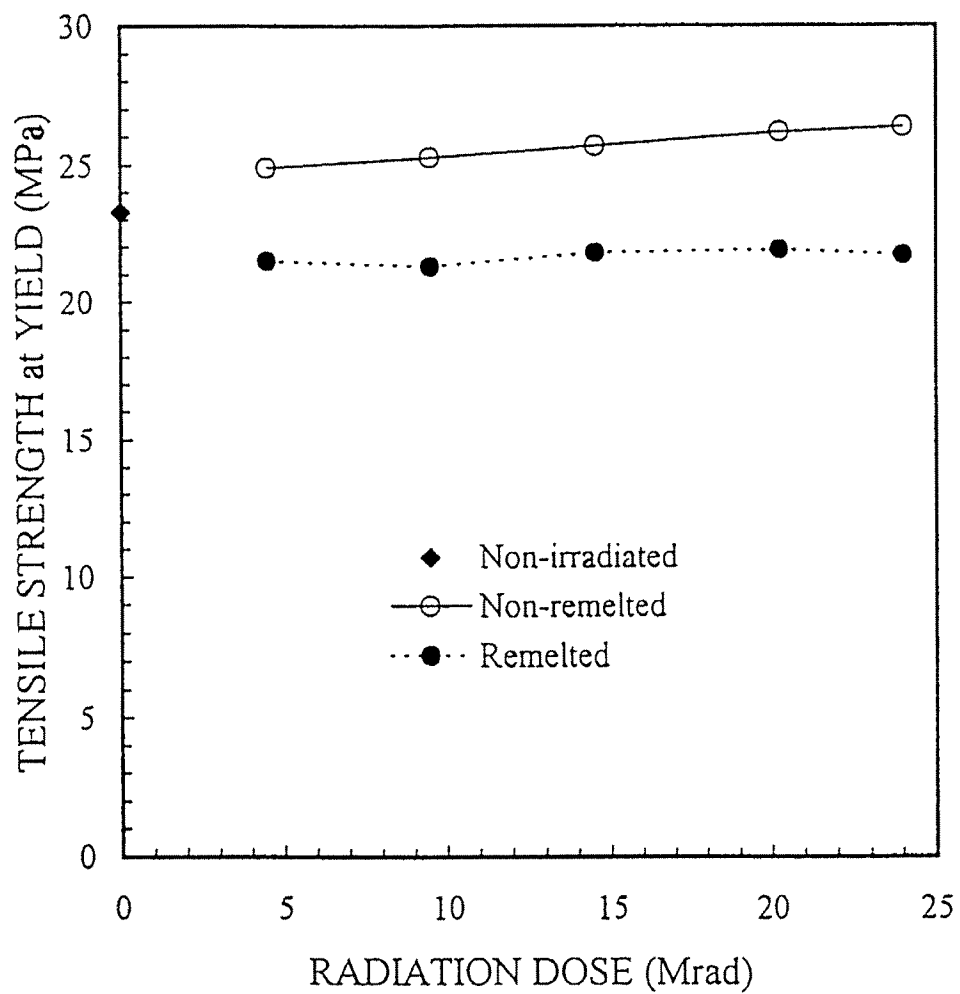
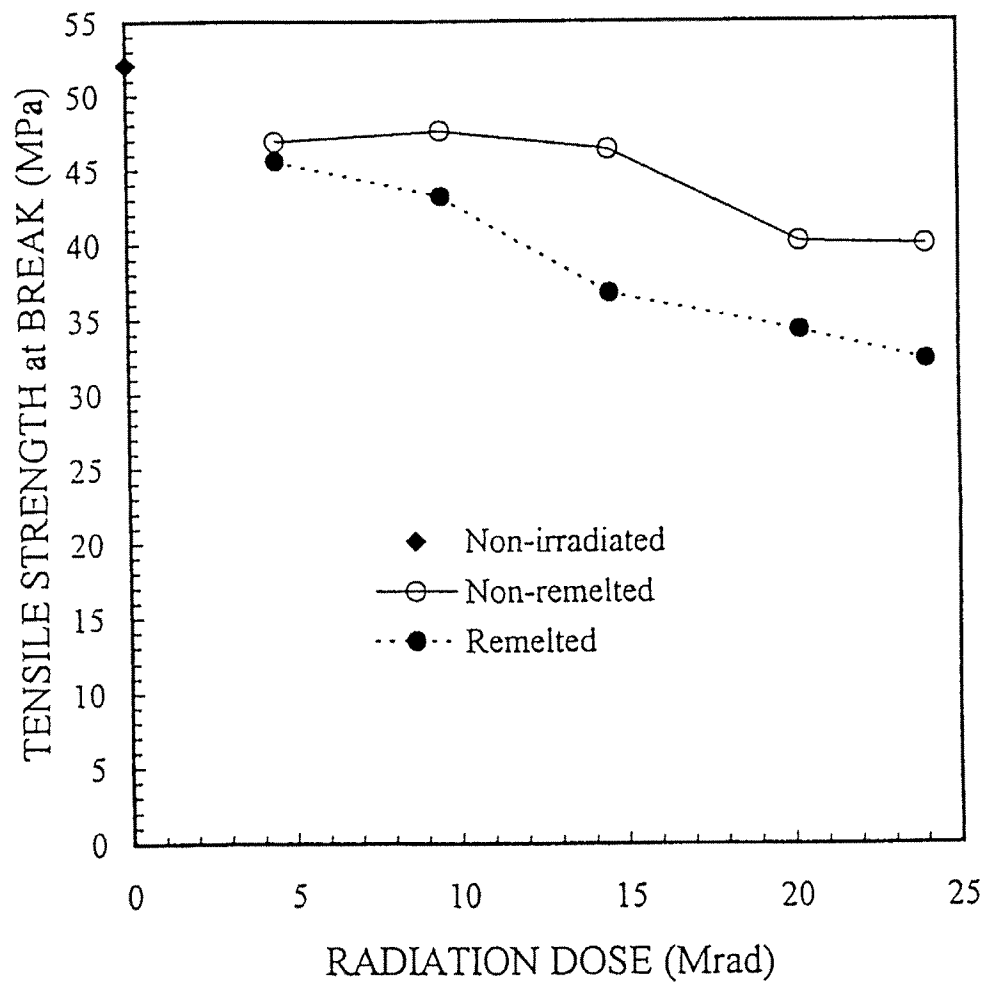


FIG. 25

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**FIG. 26**

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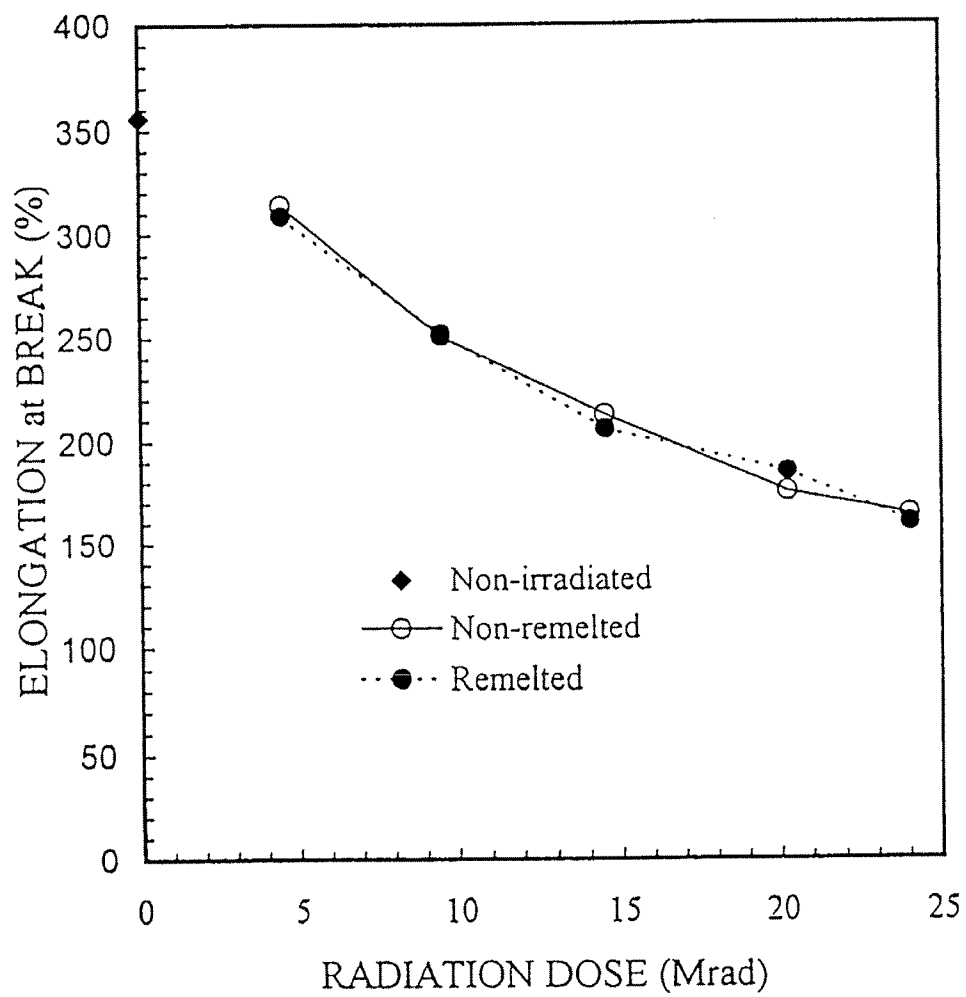


FIG. 27

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/11947

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61F 2/00, 2/32, 2/34; C08J 3/28, 5/16; C08F 110/02, 110/06.

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 522/153, 161, 163, 164; 523/113, 115; 525/937; 526/351, 352; 623/18, 19, 20, 21, 22, 23.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,281,420 A (RAAB) 04 August 1981, Abstract, column 3, lines 19-40, column 5, lines 15-62, column 6, line 34, to column 7, line 11, Examples 2 and 6.	1, 5-7, 10, 13, 15, 16, 21, 23-25, 28-30 ----- 2-4, 8, 9, 11, 12, 14, 17-20, 22
A	US 4,055,862 A (FARLING) 01 November 1977, Abstract, column 4, lines 1-51.	1-30
X --- Y	US 5,439,949 A (LUCAS ET AL) 08 August 1995, column 3, line 41, to column 4, line 34, column 6, lines 1-11, Example 1.	1, 6, 8, 15, 17, 28, 30 ----- 2-5, 7, 9-14, 16, 18-27, 29

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
31 OCTOBER 1997Date of mailing of the international search report
28 NOV 1997Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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Telephone No. (703) 308-1235

INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	US 5,577,368 A (HAMILTON ET AL) 26 November 1996, column 3, lines 35-53, column 4, lines 8-16, column 4, line 63, to column 5, line 4, column 5, lines 39-64, Examples 1-4.	1-30
Y	US 5,210,130 A (HOWARD, JR.) 11 May 1993, column 2, line 49, to column 3, line 17, column 5, lines 30-34.	1-30
Y	US 4,582,656 A (HOFFMAN) 15 April 1986, column 1, line 59, to column 2, line 28, Example 1.	1-30
X ---- Y	US 5,200,439 A (ASANUMA) 06 April 1993, column 3, line 27, to column 4, line 5, Examples 1-6.	1-4, 6, 8, 9, 12, 15, 17, 18, 23, 28, 30 ----- 5, 7, 10, 11, 13, 14, 16, 19, 24-27, 29
X --- Y	US 2,948,666 A (LAWTON) 09 August 1960, column 2, line 55, to column 3, line 23, column 4, lines 47-66, Examples.	1, 6, 8, 13, 15, 17, 21, 23, 28, 30 ----- 2-5, 7, 9-12, 14, 16, 19, 20, 22, 24-27, 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/11947**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/11947

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

522/153, 161, 163, 164; 523/113, 115; 525/937; 526/351, 352; 623/18, 19, 20, 21, 22, 23.

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS: prosthetic or artificial joints, acetabular, hip, in vivo implants, bearing surfaces, moving contact, sliding, pivoting, rotating, UHMWPE, HIFAX 1900, GUR 4020, 4120, 4150, polymethylmethacrylate, nylon, polycarbonate, polyethylene, polypropylene, irradiation, photocrosslinking, crystallinity, gel content

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-25, drawn to a thermally treated crosslinked polymer, method of preparing the polymer and in vivo implant comprising the polymer.

Group II, claim(s) 26-30, drawn to a method for determining optimal radiation dose and thermal treatment for treating a polymer and to the product produced.

The inventions listed as Groups I-II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: (1) the steps for determining radiation dose and remelting or annealing conditions set forth in the claims of Group II are not required in the method set forth in the claims of Group I (2) the characteristics of the polymeric composition set forth in the claims of Group I are not mentioned in the claims of Group II.

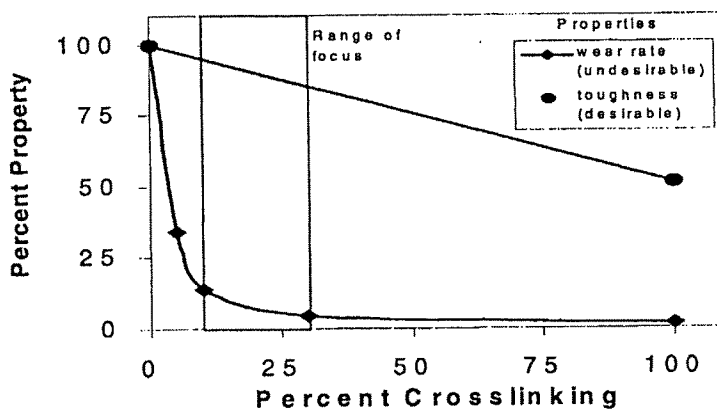


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : A61F 2/30		A1	(11) International Publication Number: WO 00/62717
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(21) International Application Number: PCT/US00/10673 (22) International Filing Date: 20 April 2000 (20.04.00) (30) Priority Data: 60/130,322 21 April 1999 (21.04.99) US (71) Applicant: STRYKER TECHNOLOGIES CORPORATION [US/US]; 2725 Fairfield Road, Kalamazoo, MI 49002 (US). (72) Inventors: WANG, Aiguo; 432 Marlboro Road, Wood-Ridge, NJ 07075 (US). ESSNER, Aaron, Paul; 30 Vreeland Avenue, Bloomingdale, NJ 07403 (US). ZARNOWSKI, Alfred, J.; 362 West End Avenue, North Plainfield, NJ 07063 (US). (74) Agents: GILMAN, Keith, E. et al.; Lerner, David, Littenberg, Krumholz & Mentlik, LLP, 600 South Avenue West, Westfield, NJ 07090 (US).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	

(54) Title: SELECTIVELY CROSS-LINKED POLYETHYLENE ORTHOPEDIC DEVICES

Effect of Selective-Crosslinking on Toughness and Wear Rate



(57) Abstract

An improved prosthetic medical device having improved wear resistance and toughness is provided in the present application. A method is provided to selectively cross-link the polymeric matrix comprising the medical device by employing an interrupting means such as a mask, wire mesh or chopper wheel placed in between the medical device and irradiation source. In addition, the medical device may be translated while being irradiated to further effect the selective cross-linking. The present invention also provides for an injection molding process wherein a prosthetic medical device is formed in a single step, then selectively cross-linked.

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SELECTIVELY CROSS-LINKED POLYETHYLENE ORTHOPEDIC DEVICES

FIELD OF THE INVENTION

This invention relates generally to producing prosthetic medical devices. More specifically, the invention provides methods to produce compositions made of polyethylene which have been irradiated in such a manner so that only a selected percentage of the overall composition has been allowed to cross-link. The capability to precisely control the degree and location of cross-linking in a polymer has particular advantages in the orthopedic device arts.

BACKGROUND OF THE INVENTION

Many prosthetic medical devices are implanted into load-bearing joints such as knees, hips, etc. As such, these prosthetic devices must be very strong and possess a high degree of wear resistance. The prosthetic medical device industry has utilized various methods and compositions employing metals and polymers and combinations thereof to fabricate prosthetic devices. Prosthetic medical devices manufacturers constantly work toward developing better products by improving their physical properties. Improved wear resistance, for example, is a desirable quality to impart to a prosthetic medical device. Improving wear resistance without losing strength or causing oxidative degradation is a difficult balance to obtain.

Various methods of manufacturing compositions of polymeric materials have been devised with the objectives of reducing wear rate and improving the oxidation resistance of the polymeric materials used to fabricate prosthetic medical devices. U.S. Patent Nos. 6,017,975, 5,879,400, 5,414,049 and 5,728,510 are referenced herein to illustrate the common methods and compositions used to fabricate polymeric prosthetic devices presently employed in the field.

One common practice within the prosthetic medical device industry is to use cross-linked polymers and resins to form the medical device. "Cross-linked" polymers are defined as polymeric materials which have been subjected to chemical or radiation-initiated activation resulting in dendritic bond formation between and amongst individual polymeric chains yielding new intermolecular and intramolecular networks. These cross-linked networks within the polymer provide chemical and physical properties which are usually different from the virgin polymer. Such properties include increased wear and creep resistance, durability, etc. Indiscriminate or uncontrolled cross-linking of the polymeric material comprising the

prosthetic device may result in improved wear resistance, but strength and other desirable properties may be sacrificed.

Another difficulty conventionally encountered in the manufacturing process of polymeric components of ball and socket or bearing-type prosthetic medical devices, such as hips, knees, and other load-bearing joints, is that they cannot be formed easily by inexpensive injection molding techniques. Instead, these particular types of prostheses must first be formed into a stock bar or rod, by extrusion for example, after which further machining is necessary to form the finished article. Injection molding, on-the-other-hand, allows for the final article to be formed in virtually one step.

Therefore, a need exists within the prosthetic medical device industry to fabricate an improved polymeric prosthetic device possessing sufficient strength to withstand the stress and pressure imposed on it, yet resist wear. There also exists a need to fabricate the devices inexpensively by injection molding. The present invention provides compositions, as well as methods of improving the wear resistance of prosthetic medical devices, by selectively cross-linking a polymeric resin using a controlled cross-linking process providing improved strength and wear resistance.

The present invention also provides compositions and methods of injection molding and selectively cross-linking prosthetic medical devices thus rendering an inexpensive, and more facile prosthetic medical device fabrication process.

SUMMARY OF THE INVENTION

The present invention provides methods of producing selectively cross-linked polyethylene orthopedic devices. Specifically, the invention provides a localized and controlled cross-linking method used to produce orthopedic implant prosthesis having improved wear characteristics. The localized and controlled degree of cross-linking is accomplished by exposing a polyethylene object or pre-formed orthopedic prosthetic joint or limb bearing surface to an interrupted, masked or pulsed radiation source. The interrupted radiation source may be accomplished by various means, all of which limit the amount of radiation ultimately contacting the object. By interrupting or limiting the radiation exposure to certain sites on the polyethylene object or prosthetic device, cross-linking only occurs where the radiation is able to contact or penetrate the object. Other areas not so contacted with the radiation either do not become cross-linked or only peripherally so. The invention therefore, allows a technician not only to control where the cross-linking will take place within or on the

surface of a workpiece, but also the degree to which the polymer ultimately becomes cross-linked. By limiting or selectively cross-linking the polymeric device, one can impart specific desirable properties to the polymer not normally present in the raw polymer or in the fully cross-linked polymer of the prior art.

5 It is therefore one aspect of the invention to provide a process for preparing an orthopedic device by preferably providing a polyethylene workpiece such as a stock bar or rod, or alternatively, a pre-formed joint or limb bearing. The polyethylene workpiece is then positioned in the path of a radiation beam. Preferably, a beam interrupter is placed between the workpiece and the beam source. The radiation source is then activated so that the beam is cast
10 toward the workpiece but preferably interrupted partially by the interrupting means. The workpiece is preferably exposed to the interrupted radiation beam for a certain amount of time known to produce the desired amount of cross-linking. The degree of cross-linking imparted to the workpiece may correspond to a specific degree of mechanical toughness and wear resistance in the finished prosthesis.

15 The present invention provides for the fabrication of various types of prosthetic devices. While the invention is not limited to any particularly shaped prosthetic device, the preferred shapes include acetabular cups, knees, ankles, shoulders, tibial and femoral joints, finger and thumb members, vertebra, elbows, foot and toe members and wrist members.

In another aspect of the invention the polymeric materials used to form the prosthetic
20 device may selected from the group of polyethylenes including, but not limited to, high molecular weight polyethylene (HMWPE), ultra high molecular weight polyethylene (UHMWPE), high density polyethylene (HDPE), ultra high density polyethylene (UHDPE), cross-linked polyethylene and non-cross-linked polyethylene. In this aspect of the present invention, any combination of polymers listed above, or their equivalents, may be used. A
25 preferred polymer of the invention is UHMWPE, and a preferred combination is UHMWPE and HDPE.

It is another aspect of the invention to provide a mask, shield or screen to serve as the interrupting means. The mask may preferably be a perforated sheet preferably made of metal, graphite or other thermally stable equivalent material. The number of perforations would
30 preferably correspond to the ultimate exposure, and therefore the cross-linking of the workpiece. Another interrupting means may preferably be a wire mesh which would also limit the amount of radiation ultimately reaching the workpiece depending on the mesh size of the

sheet. It is preferable to practice the present invention with individual interrupting devices, however, any combination may be used.

It is another aspect of the present invention to provide a curved interrupting means, preferably a perforated sheet or wire mesh sheet. The curved sheet or mask may partially or
5 completely surround the workpiece but in either case provide partial shielding of the radiation beam to the workpiece, and thus serve as an interrupting means. The curved sheet or mask may be contoured to match the surface of a prepared polymeric workpiece or preformed prosthetic device such as, for example, an acetabular cup or tibial member.

Yet another aspect of the present invention is to provide a rotating chopper wheel
10 serving to interrupt the beam intermittently, thereby introducing cross-linking to specific areas or regions of the workpiece.

Another object of the invention is to provide a pulsed radiation beam, thereby limiting the degree of radiation ultimately contacting the workpiece.

The present invention also provides a method of irradiating a workpiece using a
15 plurality of radiation sources. The radiation sources may preferably be directed in the same or different directions, all contacting the workpiece.

It is yet another aspect of the invention to provide a method whereby the workpiece is preferably completely surrounded by an interrupting means, preferably a perforated cage, whereby a preferably plurality of radiation sources are directed to the workpiece from various
20 directions to provide an all-encompassing and uniform radiation exposure to the workpiece.

It is yet another aspect of the invention to rotate or otherwise translate the workpiece while it is exposed to the interrupted radiation beam.

In another aspect of the invention, the workpiece and/or the interrupting means such as a perforated mask or wire mesh is vibrated while in the path of the radiation beam.

It is yet another aspect of the invention to form a prosthetic device or pre-formed article
25 by injection molding which is suitable for ball and socket and bearing-type prosthetic joints.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts a graphic representation of the effects of selective cross-linking polyethylene on wear rate and toughness.

30 FIG. 2 depicts a representation of the path of an interrupted irradiation beam and the cross-linked zones created by the irradiation in the polyethylene workpiece. The distribution of the cross-linking within the zone is also demonstrated.

FIG. 3 depicts a representation of ultimate tensile strength versus percent cross-linking

FIG. 4 depicts a representation of knee wear rate versus percent cross-linking.

FIG. 5 depicts a representation of elongation versus percent cross-linking.

FIG. 6 depicts a representation of hip wear rate versus percent cross-linking.

5 FIG. 7 depicts a representation of knee wear rate versus radiation composite dose equivalent dose.

FIG. 8 depicts a representation of the general process of fabricating a prosthetic medical device according to the present invention.

10 FIG. 9 depicts a workpiece positioned under a perforated mask or shield whereby a visible light is shown to demonstrate the path and pattern of a radiation beam during operation of the present invention.

FIG. 10 depicts selectively cross-linked patterns formed within and around a polymer workpiece with and without rotation.

FIG. 11 depicts selectively cross-linked patterns formed by rotation of the workpiece.

15 FIG. 12 depicts the use of a curved perforated mask used to irradiate a workpiece.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention provides a desirable balance of improved wear resistance and high tensile strength and toughness in the polymeric compositions used for prosthetic implants. It has been discovered that wear resistance can be improved without sacrificing other desirable properties such as toughness or strength by controlling the amount of cross-linking of the polymeric substrate comprising the prosthetic device. Referring to FIG. 1, whereby the wear rate and toughness are graphically illustrated to be optimized at about 5 to 30% cross-linking. The present invention also provides that not only is the degree of controlled cross-linking useful in providing the desired properties, but also the localized positioning of the cross-linked phase of the polymer within the matrix. Thus, the above noted percentage of cross-linking may be distributed uniformly over the entire surface area, and/or within the matrix, of the workpiece, or may comprise a specific pattern of cross-linking, depending upon the ultimate use of the finished prosthetic device.

25 The practice of the present invention has resulted in improved wear reduction with less loss of mechanical properties, as compared to bulk cross-linked prosthetic devices. Thus the essence of the present invention is to control the degree and location of the cross-linked phase

30

of the polymer within the matrix of the prosthetic device or stock work piece which results in a desirable balance of properties between wear resistance and toughness.

This balance, and therefore the polymeric selectivity in cross-linking, of the present invention is achieved by virtue of interrupted irradiation exposure of the polyethylene article to effectuate a selected pattern and percentage of cross-linking in the article being treated. This process is termed "selective cross-linking." As will be described in detail below, the interruption in the irradiation exposure of the work piece is accomplished by various means. For illustrative purposes, such means may preferably be a perforated mask, wire mesh, chopper wheel, or other device capable of partially blocking the path of the radiation beam. See Fig.13 whereby a workpiece is positioned under a perforated mask or shield. A light is projected onto the upper surface of the mask to demonstrate the interrupted path of what the radiation beam would contact as well as the penetration pattern projected onto the workpiece. In other examples, the beam may be interrupted by pulsing the emission of the beam from the source, as well as projecting a finely focused beam, or a plurality of such, directly onto the work piece. In addition, the dose, or exposure time, of the irradiation can be varied separately or in conjunction with the use of the above-described interruption means to provide another method of controlling the level of cross-linking. For the purposes of describing the present invention, "percent cross-linking" means the fraction of overall radiation energy projected toward the workpiece which is not interrupted and thus ultimately contacts the workpiece.

Generally, to practice the present invention, a polymer workpiece is placed in the path of, or adjacent to, an irradiation beam, the beam is interrupted by an interrupting means for a desired period of time to effectuate the desired level of cross-linking. The workpiece is then annealed. Thereafter, the workpiece is shaped into a prosthetic device as necessary and packaged according to common industry processes. See FIG. 8 for a schematic representation of a typical method of processing a prosthetic device according to the present invention. The processing of the prosthetic device, after selectively cross-linking according to the present invention, may be performed by conventional methods. For example the necessary packaging, finishing, annealing, sterilizing, etc. may be practiced according to those processes disclosed and/or claimed in U.S. Patent 5,414,049, which is hereby incorporated by reference.

Prosthetic devices fabricated according to the present invention possess an improved performance profile as compared to control devices comprising 100% cross-linking. For example FIG. 3 plots ultimate tensile strength versus percent cross-linking. As illustrated,

devices possessing 10, 20 and 30 % cross-linking exhibit low levels of strength loss as compared to the control. However, FIG. 4 illustrates a desirable decrease in wear rate at the same 10, 20 and 30% cross-linking levels. In addition, FIG. 5 illustrates a minimum change of elongation, at 10, 20 and 30% cross-linking as compared to the control which is 100% cross-linked. The above data demonstrates that the selective cross-linking of the present invention provides a balance of desirable properties such as low wear rate and high mechanical toughness without the undesirable properties such as brittleness and accelerated wear rates.

Regardless of the method or device used, the present invention provides for any controlled and/or selective exposure of the work piece to a radiation beam for the purposes of limiting the degree of cross-linking within the polymeric matrix of the prosthetic device or preformed work piece. Note that the dose or exposure time of the radiation beam contributes to the overall properties of the prosthetic devices of the present invention.

The effect of the radiation dose on wear rate according to the present invention is illustrated in FIG. 6. As shown FIG. 6 demonstrates that the wear rate decreases along with the percent cross-linking at two radiation dose levels, 15 and 7.5 Mrads. FIG. 7 illustrates a comparison between conventional bulk cross-linking versus the selective cross-linking of the present invention. This is shown as a function of "composite dose" (cross-linking) in FIG. 7. The composite dose equals the percent cross-linking region multiplied by the dose received. For example, 30% of the cross-linked region is multiplied by the total dose received (15Mrads), resulting in a composite dose of 4.5 Mrads; ($0.30 \times 15 = 4.5$).

Without being limited to any particular theory to explain why or how the present invention works, the improved properties exhibited by the devices provided by the present invention may be explained as follows. The interrupting means causes specific and perhaps alternating zones of cross-linked and non cross-linked polymer to form within the matrix of the article exposed to the invention. As illustrated in FIG. 2, each cross-linked zone may possess a natural distribution of cross-linked polymer after exposure. As such, the post-exposure article could be composed of alternating zones of essentially two or more different polymers (by different we mean different cross-linking percentages) made so by the interrupted irradiation.

These different polymers may separately contribute to the overall physical properties of the resulting polymeric article. For example, the highly cross-linked zones may possess a high degree of strength, as is typically seen from most cross-linked polymers. A non cross-linked zone, may contribute a certain degree of pliability and flexibility. Because the different

polymers are integrally networked within the polymer, a synergistically improved material results possessing many desirable properties such as wear resistance and toughness, without the undesirable aspects either of such properties normally includes when only individually present.

5 Another possible theory for the unexpected results of the present invention is set forth as follows. In a polymer matrix made according to the present invention whereby alternating cross-linked and non cross-linked zones have been formed, the non cross-linked zones exhibit a minor surface compression phenomenon whereby the termini of each non cross-linked zone depresses within the matrix due to its more pliable nature. The termini of the cross-linked
10 zones, however, would not be as flexible or compressible, and therefore would not compress. If this is correct, the surface of a prosthetic joint made according to the present invention would in effect allow objects pressed to its surface to "ride" on a series of undulating cross-linked termini not unlike a series ball bearings. As such, less surface contact by an abutting bone or another prosthetic joint is made thereby minimizing the wear rate of the prosthetic
15 device. The above described contact of undulated surfaces may also facilitate fluid entrapment and thus enhance lubrication. This proposed surface phenomenon could provide significant wear reduction to the limited overall surface contacted, but retain structural integrity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one embodiment of the present invention, the polymer utilized to make up the
20 prosthetic device or work piece may be selected from the group of polyethylenes including, but not limited to, high molecular weight polyethylene (HMWPE), ultra high molecular weight polyethylene (UHMWPE), high density polyethylene (HDPE), ultra high density polyethylene (UHDPE), cross-linked polyethylene and non-cross-linked polyethylene. The preferred polyethylene species of the present invention is UHMWPE. However, combinations of any or
25 all of the above listed polymers, along with any equivalent polymer, may be combined to practice the present invention. The UHMWPE used in the present invention may preferably have a molecular weight between about 1,000,000 to about 10,000,000, in a more preferred embodiment, the molecular weight is between about 2,000,000 and 6,000,000. The HDPE used in the present invention may preferably have a molecular weight between about 1,000 to
30 1,000,000. In an even more preferred embodiment, the molecular weight is between about 200,000 to 500,000.

In another embodiment of the present invention, a desirable balance of toughness and wear rate in polyethylene is achieved when the cross-linking percentage is within the range of between about 1-90% selectively cross-linked. In a more preferred embodiment of the present invention, the selectively cross-linked percentage is between about 2.5-50%. Even more preferred is a selectively cross-linked range of between about 5 to 30%, as illustrated in FIG. 1. Of course, this range may differ depending upon the particular device and its size, shape and intended use as well as the type of polyethylene comprising the device.

Another embodiment of the present invention provides for the mixture of polyethylenes. One particularly preferred embodiment includes a mixture of HDPE and UHMWPE. A preferred ratio of HDPE to UHMWPE is 50:50, and even more preferred ratio is 60:40, and the most preferred ratio is 70:30 HDPE to UHMWPE. This particular blend of polyethylenes exhibits unexpectedly favorable flow properties conducive to injection molding. A prosthetic device fabricated via injection molding and subjected to selective cross-linking, according to the present invention, provides an economically beneficial alternative to a more elaborate multi-step process requiring machining and finishing an extruded stock bar or rod.

Generally, the selective or controlled cross-linking of the present invention is accomplished by interrupting the exposure of the device to the irradiated beam. Several methods and devices may be employed to interrupt the irradiation beam. The irradiation may be fully or partially interrupted or intermittently interrupted in order to control exposure and dosage. The direction of any irradiation may also be controlled by employing a variety of methods and devices described below. The number of irradiation beams used on a particular device may also be varied so that a plurality of beams are simultaneously exposing, and therefore cross-linking, the polymeric matrix of the device.

One such method employs a perforated mask or shield placed partially or fully between the irradiation source and the polyethylene object. (See FIGS. 2, 9 11 and 12) The use of the perforated mask allows only certain zones of the polymer to become cross-linked. The zones that are not exposed to the irradiation do not become cross-linked. The perforated mask may be flat or curved to allow for the desired angle of inflection of the irradiation beam on the article being cross-linked (See FIGS. 2 and 14, respectively).

Another method of the present invention of interrupting the irradiation during the cross-linking process is to place a propeller or chopper wheel in between the irradiation source and the article being irradiated. An additional step to effectuate a synchronized translation or

rotation of either the article or the irradiation source may also be performed concurrently with the propeller or chopper wheel interrupting step. These methods also provide for a controlled amount of irradiation to be exposed on the article in a pre-arranged pattern. The result is a selectively cross-linked article having the desired properties described above.

5 Yet another embodiment of the present invention provides a method of interrupting the irradiation by pulsing the energy from the irradiation source. An additional step to effectuate a synchronized translation of either the article or the irradiation source may also be performed may also be performed concurrently with the interrupting step. These methods also provide for a controlled amount of irradiation to be exposed on the article in a prearranged pattern. The
10 result is a selectively cross-linked article having the desired properties described above.

In still another embodiment of the invention, the article being cross-linked can be translated, rotated, vibrated, etc., during or in between the irradiation step or steps in order to control exposure, dosage and directionality of the irradiation on the article. Such control may be desirable depending upon the ultimate use of the article. For example, an article may be
15 first exposed to an interrupted irradiation beam to produce a selectively cross-linked pattern in a particular direction. The article may then be rotated so that when the irradiation source is resumed, the exposure of the interrupted beam creates a selectively cross-linked pattern in another direction. The end result would be for example a cross-hatched pattern of cross-linked zones within and on the surface of the workpiece. See FIGS. 10 and 11. This method may be
20 termed multi-directional selective cross-linking. Such a process would render the article useful in applications where a multi-directional array of force is imposed on the article, e.g., in an acetabular cup or liner component of a hip joint replacement prosthesis as shown in FIG. 10.

In another embodiment the workpiece or pre-formed medical device may be vibrated while being subjected to selective cross-linking through any of the methods described herein.

25 In another embodiment of the invention, the device to be selectively cross-linked is positioned inside a perforated housing and exposed to at least one irradiation source. Where a plurality of irradiation sources is used, the device is exposed to irradiation in multiple directions.

The following embodiments are intended to illustrate the capability of the selective
30 cross-linking invention. The methods so described are illustrative only and should not be interpreted as constituting any limitations on the methods in accordance with the present invention.

In one embodiment, a polyethylene workpiece or orthopedic implant preform is irradiated in such a way that portions of the workpiece or orthopedic implant preform are not cross-linked. In one aspect of this embodiment, the irradiation source is fully or partially interrupted or intermittently interrupted.

5 In a preferred embodiment of the invention a seven step process is employed to selectively cross-link a polyethylene workpiece. In the first step, a polyethylene article comprised of UHMWPE in the form of a rod, bar, implant-preform or acetabular cup, tibial or patellar component is formed through molding, extrusion or other polymeric forming process.

10 The second step involves placing the polyethylene article under an irradiation source where an interrupting means such as a wire mesh, porous plate or other partial masking device has been placed between the irradiation source and the polyethylene component. The interrupting means is perforated so that about 30% of the irradiated energy passes through it and thus contacts the article.

15 Step three involves irradiating the component at a suitable accumulated dose between the range of 2.5 and 100 Mrads, preferably at about 5 to 15 Mrads. A preferred composite dose is between about 1 to 25 Mrads. An even more preferred composite dose is between about 2 to 10 Mrads, with the most preferred composite dose being about 4.5 Mrads. The irradiation source may be for example gamma rays, x-rays, electron beam or other radiation source. The duration of irradiation exposure is carried out for an appropriate time, depending
20 upon the dose rate and the desired total dose. For example, a calibration curve may be generated plotting exposure time or dose rate versus wear rate for a particular shaped article or workpiece. Thereafter, to determine the dose rate or exposure time to obtain a desired level of wear rate, one need only refer to the calibration curve for the appropriate parameters.

25 Step four involves annealing the irradiated component at an elevated temperature (below, at, or above the melting point, of polyethylene). The fifth step involves machining the irradiated component if necessary into its final shape for implantation. The sixth step involves thoroughly cleaning the finished component and placing it in a sealed package. The package may be substantially free of free oxygen and may be any container or expedient for creating and maintaining a low or zero oxygen environment. Step seven involves sterilizing the
30 packaged component with gamma, gas-plasma or ethylene oxide. In the case of ethylene oxide, the gas may be introduced in the packaging step six.

In another embodiment of the invention, a method for the production of a multi-directional cross-linked article is employed. For example, such a method comprises the method of creating multi-directional irradiation zones by exposing the article to an interrupted irradiation beam in one direction, then relocating either the irradiation beam or the article to
5 another position than the first irradiation direction, then exposing the article to the second irradiation exposure. See FIGS. 10 and 11. The repositioning step may be performed a plurality of times. An article that has been multi-directionally irradiated possesses isotropic physical properties, and is desirable for example for use as a prosthetic implant requiring multi-directional loading strength.

10 In yet another embodiment of the present invention, a polymer blend of HDPE and UHMWPE is combined and injection molded into a prosthetic device. The device is then subjected to any of the selective cross-linking methods discussed above. In a preferred embodiment, a ratio of 50:50 HDPE to UHMWPE is blended and injection molded according to conventional methods known in the art. In an even more preferred embodiment, a blend of
15 60:40 HDPE to UHMWPE is used, and most preferred is a blend of 70:30 HDPE to UHMWPE.

EXAMPLE

Several shields were produced from a 3/8 inch thick steel plate for selective cross-linking treatment of UHMWPE. The overall top surface size for each plate was approximately
20 5 inches by 5 inches square. Each shield was perforated with a series of 3 mm diameter holes in a geometric arrangement such that each perforation (hole) was equally spaced from all other perforations. One pattern involved 30% porosity or perforation. That is, 30% of the top surface area of the shield was occupied by holes uniformly distributed over the surface of the shield.
25 These parameters (3 mm hole size, equal spacing and 30% surface area) control the total number of holes as well as the inter-hole spacing. An additional shield used a 20% surface area pattern and a third used a 10% pattern.

A 3.25 inch diameter cylindrical rod of UHMWPE material was sectioned into 1.75 inch thick pieces or "pucks". This rod was made of GUR 1050 resin and was not treated or
30 cross-linked in any way. This is typically referred to as "virgin" rod. The 1.75 inch height was selected to allow uniform cross-linking through the entire thickness (height) of the puck. These pucks were then selectively cross-linked using the description that follows. See FIG. 8.

An electron beam was used to provide ionizing radiation to cross-link the UHMWPE material. This process involved exposing an UHMWPE puck to the electron beam until the desired energy was projected onto the puck.. Prior to irradiation, a perforated shield was placed between the electron beam source and the UHMWPE puck such that only the areas of the puck not covered by the shield received electron beam energy. In this way the UHMWPE puck was selectively cross-linked. See FIG. 9. The parameters used for the electron beam treatment were an absorbed 10 MeV ionizing radiation dose of 150 kiloGrays (15Mrads) at a rate of 20 kiloGrays (2Mrads) per minute so that total treatment time was 7.5 minutes. Pucks were treated using the 10%, 20% and 30% perforation shields. These pucks were then heat treated or annealed. After this step the pucks were then manufactured into knee replacement tibial inserts as well as tensile test specimens.

These tibial inserts were then tested in a knee wear simulator. This machines duplicates the motions and loading seen in a knee joint during normal walking activity. Appropriate physiological conditions were used. Results in Figure 4 show that selective cross-linking improves wear resistance over the untreated control. Details of the perforated pattern used influence performance. The tensile specimens were tested in a load frame device to yield mechanical property values, such as strength and elongation. See FIGS. 3 and 5. These values also change with the pattern. Unlike wear, it is desirable to keep these values high.

It is therefore intended that the foregoing detailed description be regarded as illustrative rather than limiting, and that it be understood that it is the following claims, including all equivalents, which are intended to define the scope of the present invention.

CLAIMS

We claim:

1. A process of preparing an orthopedic device, comprising the steps of:
 - a) providing a polyethylene workpiece; and
 - 5 b) positioning an irradiation source adjacent to the workpiece so that the workpiece may be exposed to irradiation from the irradiation source; and
 - c) interrupting the irradiation source so that only portions of the workpiece are exposed to irradiation.
2. The method of claim 1, further comprising the step of translating the workpiece.
- 10 3. The method of claim 1, further comprising the step of arranging a perforated mask between the irradiation source and the workpiece.
4. The method of claims 1, further comprising the step of arranging a wire mesh between the irradiation source and the workpiece.
5. The method of claim 3, wherein the perforated mask is curved.
- 15 6. The method of claim 4, wherein the wire mesh surrounding the workpiece is curved.
7. The method of claim 1, further comprising a rotatably mounted chopper wheel between the irradiation source and the workpiece.
8. The method of claim 1, further comprising the step of pulsing the irradiation source.
9. The method of claim 1, wherein the irradiation step is controlled to deliver a dose of
20 irradiation between 2.5 and 100 Mrads.
10. The method of claim 1, wherein the irradiation step is controlled to deliver a dose of irradiation between 5 and 15 Mrads.
11. The method of claim 1, further comprising the step of pre-forming the workpiece into a form suitable for implantation prior to the irradiation step.
- 25 12. The method of claim 11, wherein said pre-forming step comprises injection molding said workpiece into forms suitable for implantation prior to the irradiation step.
13. The method of claim 12, wherein said injection molding step is performed with a blend of UHMWPE and HDPE to form said workpiece.
14. The method of claim 12, wherein said injection molding step is performed with a blend
30 of UHMWPE and HDPE to form said workpiece, said blend having a ratio of about 30:70 UHMWPE to HDPE.

15. The method of claim 1, further comprising the step of shaping said workpiece into the forms selected from the group consisting of acetabular cups, knees, ankles, shoulders, tibial and femoral joints, finger and thumb members, vertebra, elbows, foot, toe and wrist members.

5 16. The method of claim 1, wherein the composition of the polyethylene workpiece is selected from the group comprising high molecular weight polyethylene, ultra high molecular weight polyethylene, high density polyethylene, ultra high density polyethylene, cross-linked polyethylene and non-cross-linked polyethylene.

17. The method of claim 1, wherein the polyethylene is UHMWPE.

10 18. The method of claim 17, wherein the UHMWPE has a molecular weight between about 1,000,000 to 10,000,000.

19. The method of claim 18, wherein the UHMWPE has a molecular weight between about 2,000,000 to 6,000,000.

20. A method of preparing a prosthetic orthopedic medical device, comprising the steps of:

- 15 a) providing a preformed polyethylene orthopedic device; and
b) enclosing the device in a package to provide a low oxygen content environment;
and
c) positioning an irradiation source adjacent to the packaged device so that the packaged device may be exposed to irradiation from the irradiation source; and
d) interrupting the irradiation source so that only portions of the packaged device are
20 exposed to irradiation.

21. The method of claim 20, further comprising the step of translating the packaged device.

22. The method of claim 20, further comprising the step of arranging a perforated mask between the irradiation source and the packaged device.

25 23. The method of claim 20, further comprising the step of arranging a wire mesh between the irradiation source and the packaged device.

24. The method of claim 23, wherein the perforated mask is curved.

25. The method of claim 24, wherein the wire mesh is curved.

26. The method of claim 20, further comprising a rotatably mounted chopper wheel between the irradiation source and the packaged device.

30 27. The method of claim 20, further comprising the step of pulsing the irradiation source.

28. The method of claim 20, wherein the irradiation step is controlled to deliver a dose of irradiation between 2.5 and 100 Mrads.

29. The method of claim 20, wherein the composition of the workpiece is selected from the group consisting of high molecular weight polyethylene, ultra high molecular weight polyethylene, high density polyethylene, ultra high density polyethylene, cross-linked polyethylene and non-cross-linked polyethylene.

5 30. A prosthetic medical device produced by the process comprising the steps:
a) providing a polyethylene workpiece; and
b) positioning at least one irradiation source adjacent to the workpiece so that the workpiece may be exposed to irradiation from the irradiation source; and
c) interrupting the irradiation source so that only portions of the workpiece are
10 exposed to irradiation.

31. The prosthetic medical device according to claim 30, further comprising the step of shaping said workpiece into a prosthetic device.

32. The prosthetic medical device of claim 30, wherein said polyethylene is selected from the group consisting of high molecular weight polyethylene, ultra high molecular weight
15 polyethylene, high density polyethylene, ultra high density polyethylene, cross-linked polyethylene and non-cross-linked polyethylene.

33. The prosthetic medical device of claim 30, wherein said polyethylene is UHMWPE.

34. The prosthetic medical device of claim 30, wherein said polyethylene is a blend of UHMWPE and HDPE blended in a ratio of about 50:50.

20 35. The prosthetic medical device of claim 30, wherein said polyethylene is a blend of UHMWPE and HDPE blended in a ratio of about 30:70 UHMWPE to HDPE.

36. The prosthetic medical device of claim 30, wherein said irradiation is interrupted by a perforated mask.

25 37. The prosthetic medical device of claim 30, wherein said irradiation is interrupted by a wire mesh.

38. The prosthetic medical device of claim 30, wherein said irradiation is interrupted by a chopper wheel.

39. The prosthetic medical device of claim 30, wherein said irradiation is interrupted by a curved mask.

30 40. The prosthetic medical device of claim 30, wherein said workpiece exposure to irradiation is provided at a dose of between about 2.5 to 100 Mrads.

41. The prosthetic medical device of claim 30, wherein said workpiece exposure to irradiation is provided at a dose of between about 5 to 25 Mrads.

42. The medical device of claim 30, wherein said workpiece exposure to irradiation is provided at a dose of between about 10 to 20 Mrads.

5 43. The medical device according to claim 30, further comprising the step of translating said workpiece.

44. A prosthetic orthopedic medical device comprising a selectively cross-linked polyethylene polymer.

10 45. The prosthetic orthopedic medical device of claim 44, wherein said polyethylene is selected from the group comprising high molecular weight polyethylene, ultra high molecular weight polyethylene, high density polyethylene, ultra high density polyethylene, cross-linked polyethylene and non-cross-linked polyethylene.

46. The prosthetic orthopedic medical device of claim 44, wherein said polyethylene is UHMWPE.

15 47. The prosthetic orthopedic medical device of claim 46, wherein said UHMWPE has a molecular weight between about 1,000,000 to 10,000,000.

48. The prosthetic orthopedic medical device of claims 46, wherein said UHMWPE has a molecular weight between about 2,000,000 to 6,000,000.

20 49. The prosthetic orthopedic medical device according to claim 44, wherein said polyethylene is HDPE.

50. The prosthetic orthopedic medical device according to claim 49, wherein said HDPE has a molecular weight between about 1,000 to 1,000,000.

51. The prosthetic orthopedic medical device according to claim 49, wherein said HDPE has a molecular weight between about 200,000 to 500,000.

25 52. The prosthetic orthopedic medical device according to claim 44, wherein said polyethylene is a blend of UHMWPE and HDPE.

53. The prosthetic orthopedic medical device according to claim 52, wherein said polyethylene blend of UHMWPE and HDPE is mixed in a ratio of about 50:50.

30 54. The prosthetic orthopedic medical device according to claim 52, wherein said polyethylene blend is mixed in a ratio of 30:70 UHMWPE to HDPE.

55. The prosthetic orthopedic medical device according to any of claims 44, 52, 53, or 54 whereby said polyethylene is injection molded to form the medical device.

56. The prosthetic orthopedic medical device according claim 44, whereby said polyethylene is selectively cross-linked to a range between about 1 to 50%.

57. The prosthetic orthopedic medical device according claim 44, whereby said polyethylene is selectively cross-linked to a range between about 2.5 to 40%.

5 58. The prosthetic orthopedic medical device according claim 44, whereby said polyethylene is selectively cross-linked to a range between about 5 to 30%.

59. The prosthetic orthopedic medical device comprising a 30% selectively cross-linked injection molded polyethylene blend of 70:30 HDPE to UHMWPE.

10 60. A prosthetic orthopedic medical device comprising a 30% selectively cross-linked UHMWPE shaped into a form selected from the group consisting of acetabular cups, knees, ankles, shoulders, tibial and femoral joints, finger and thumb members, vertebra, elbows, foot, toe and wrist prosthetic components.

Effect of Selective-Crosslinking on Toughness and Wear Rate

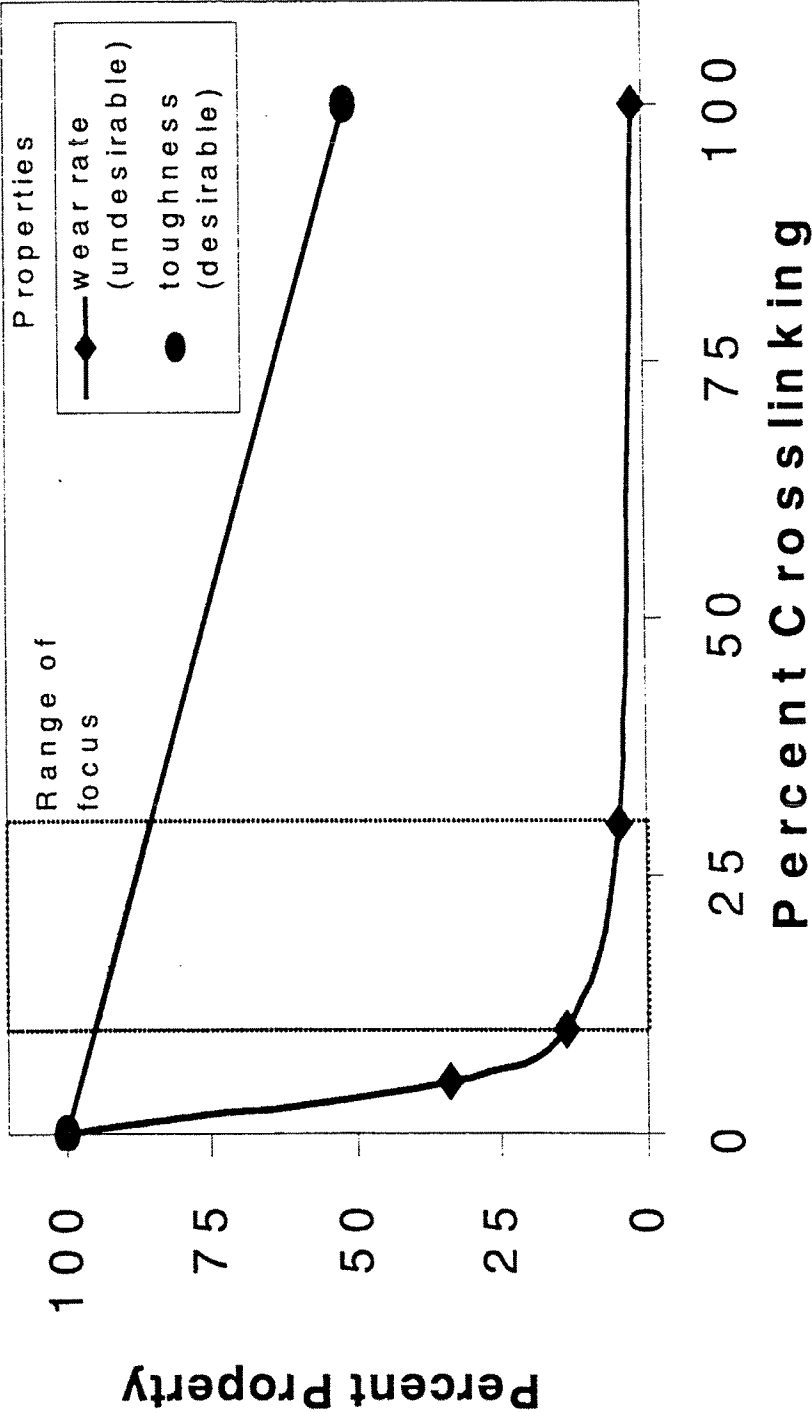


FIG. 1

Selective Crosslinking

Radiation source

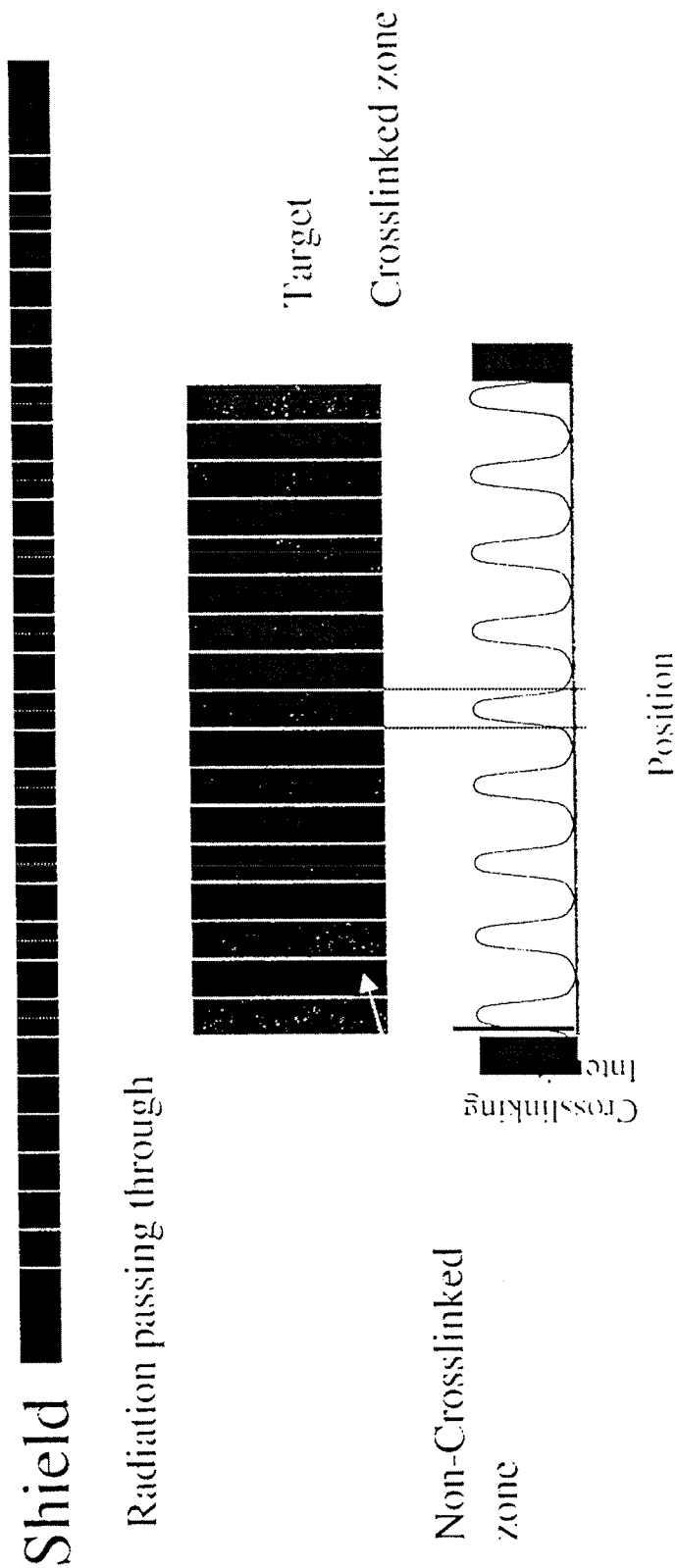


FIG. 2

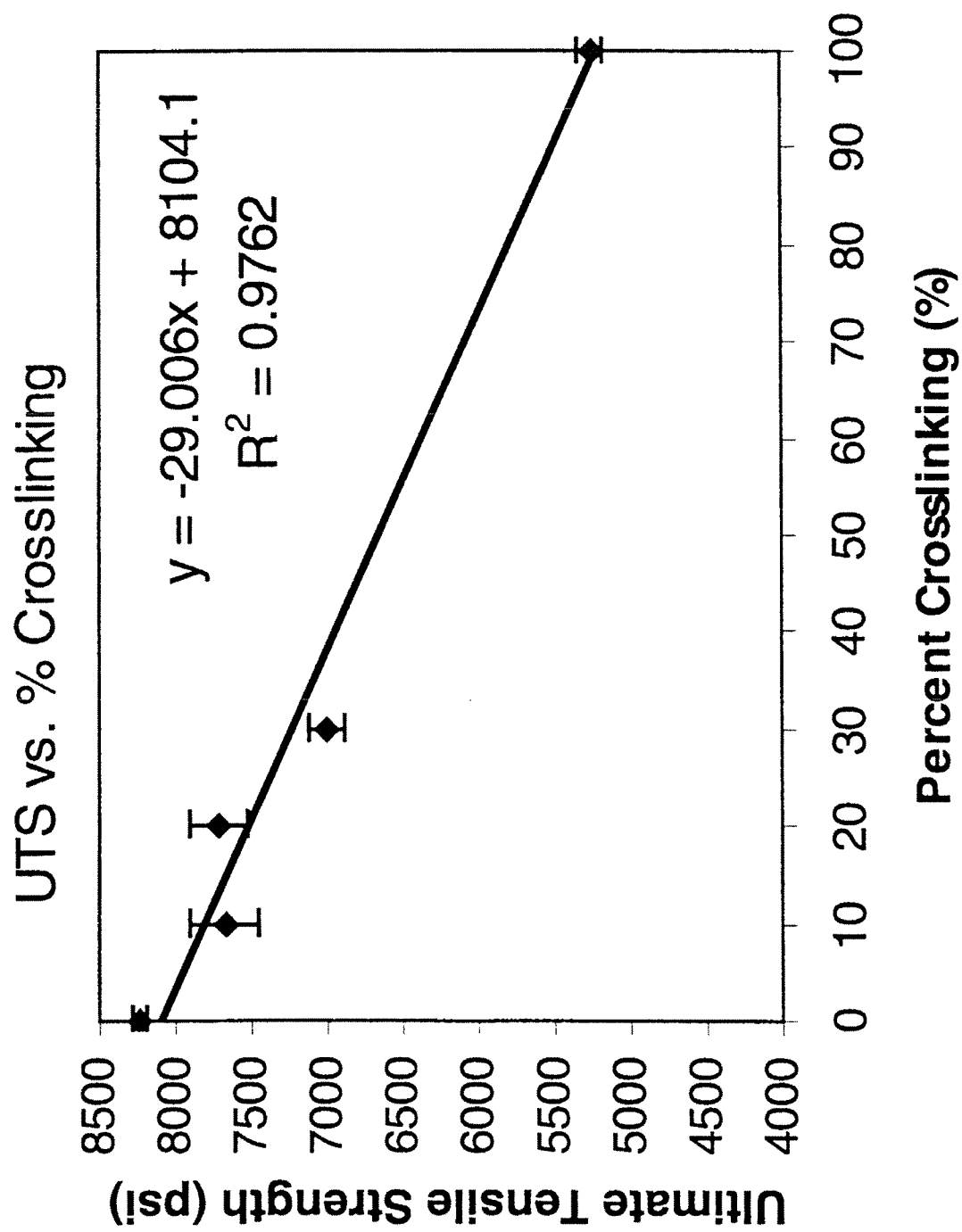


FIG. 3

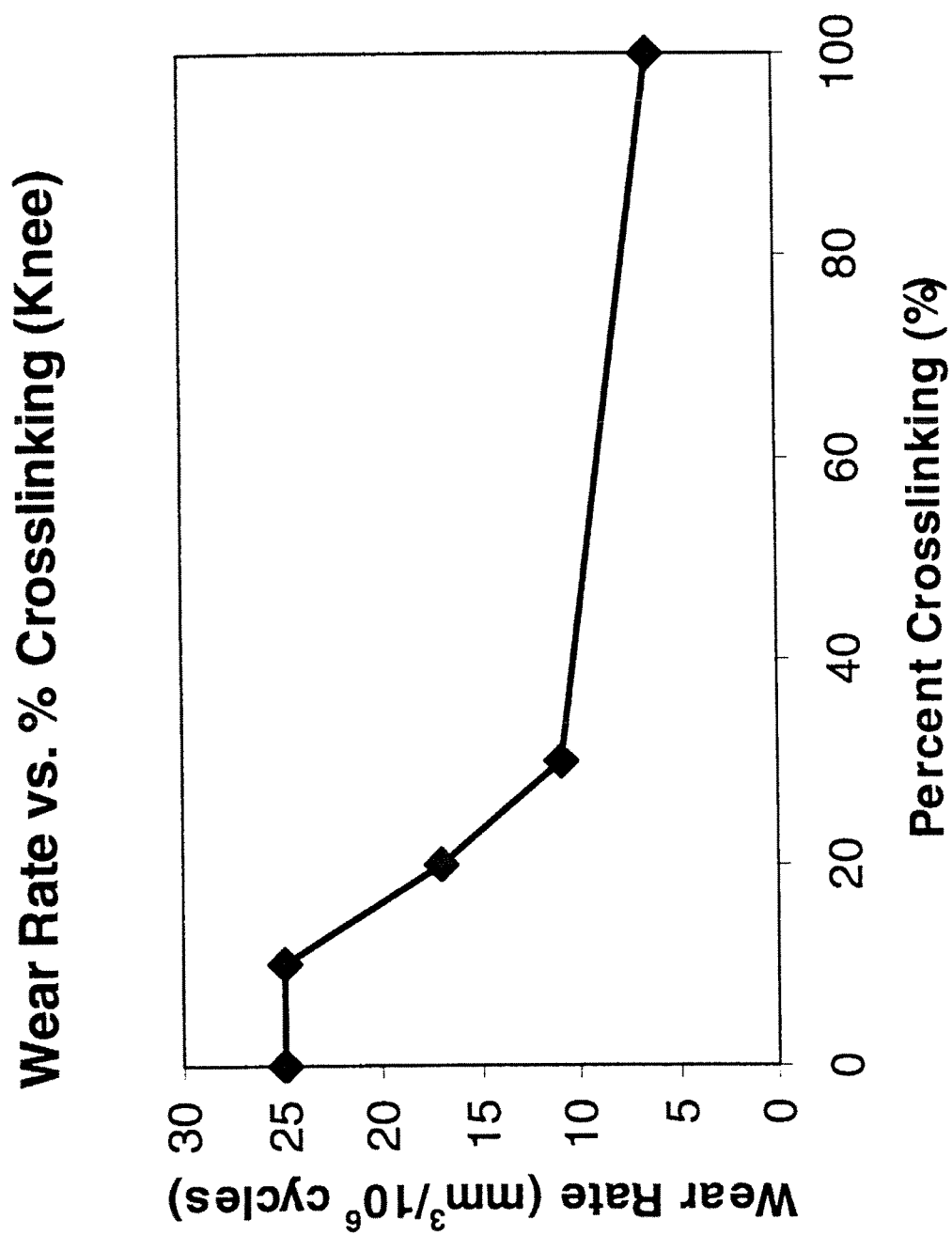


FIG. 4

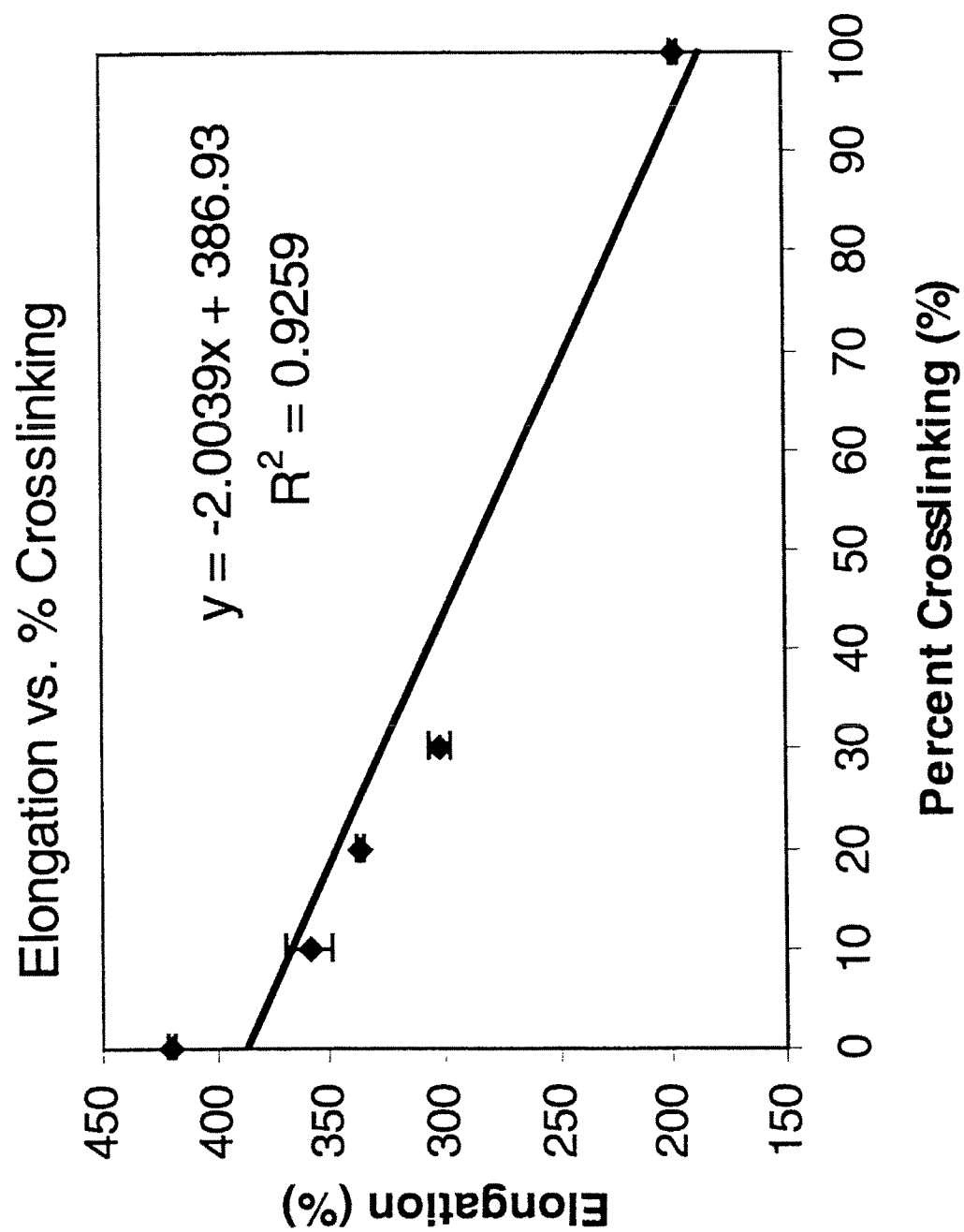


FIG. 5

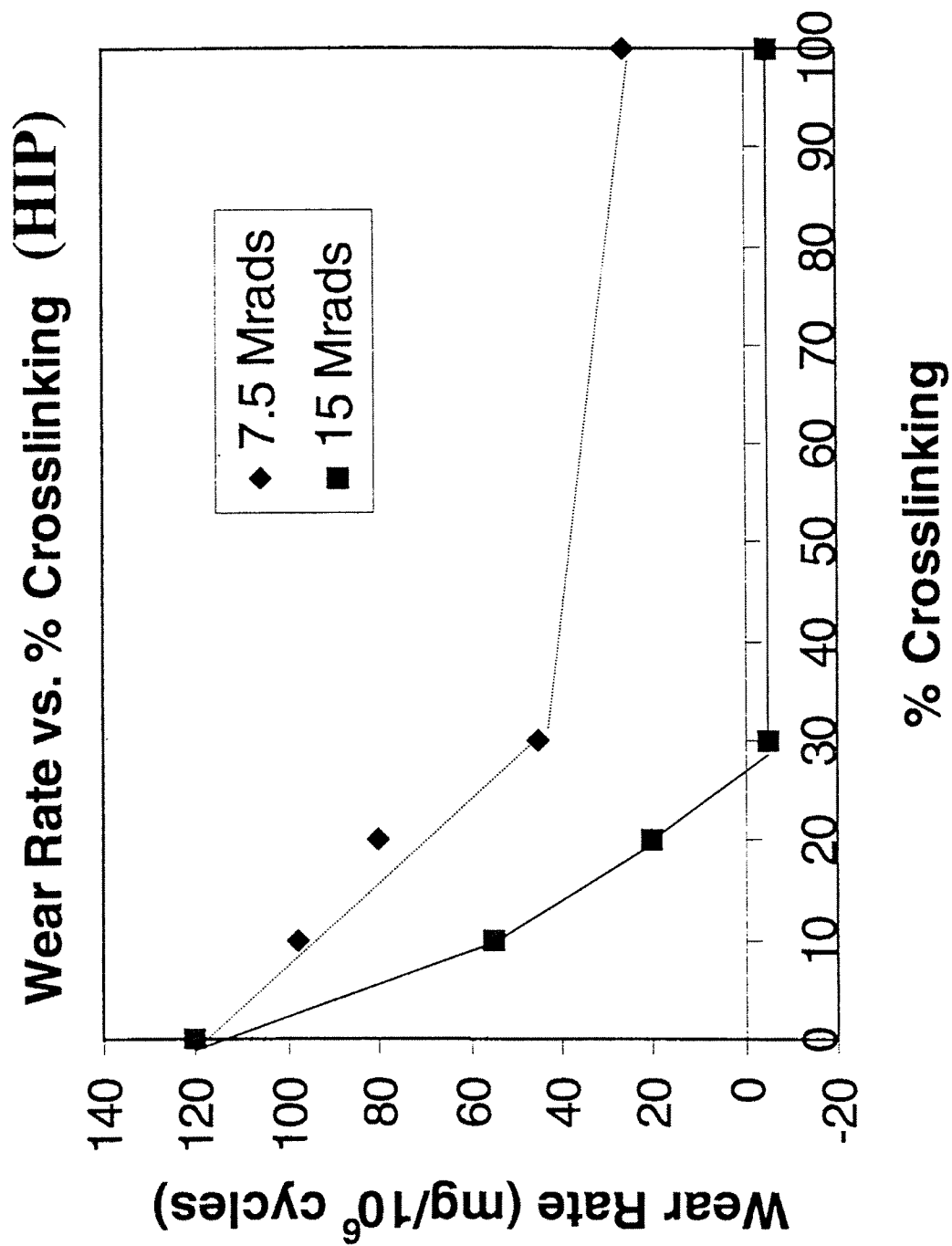


FIG. 6

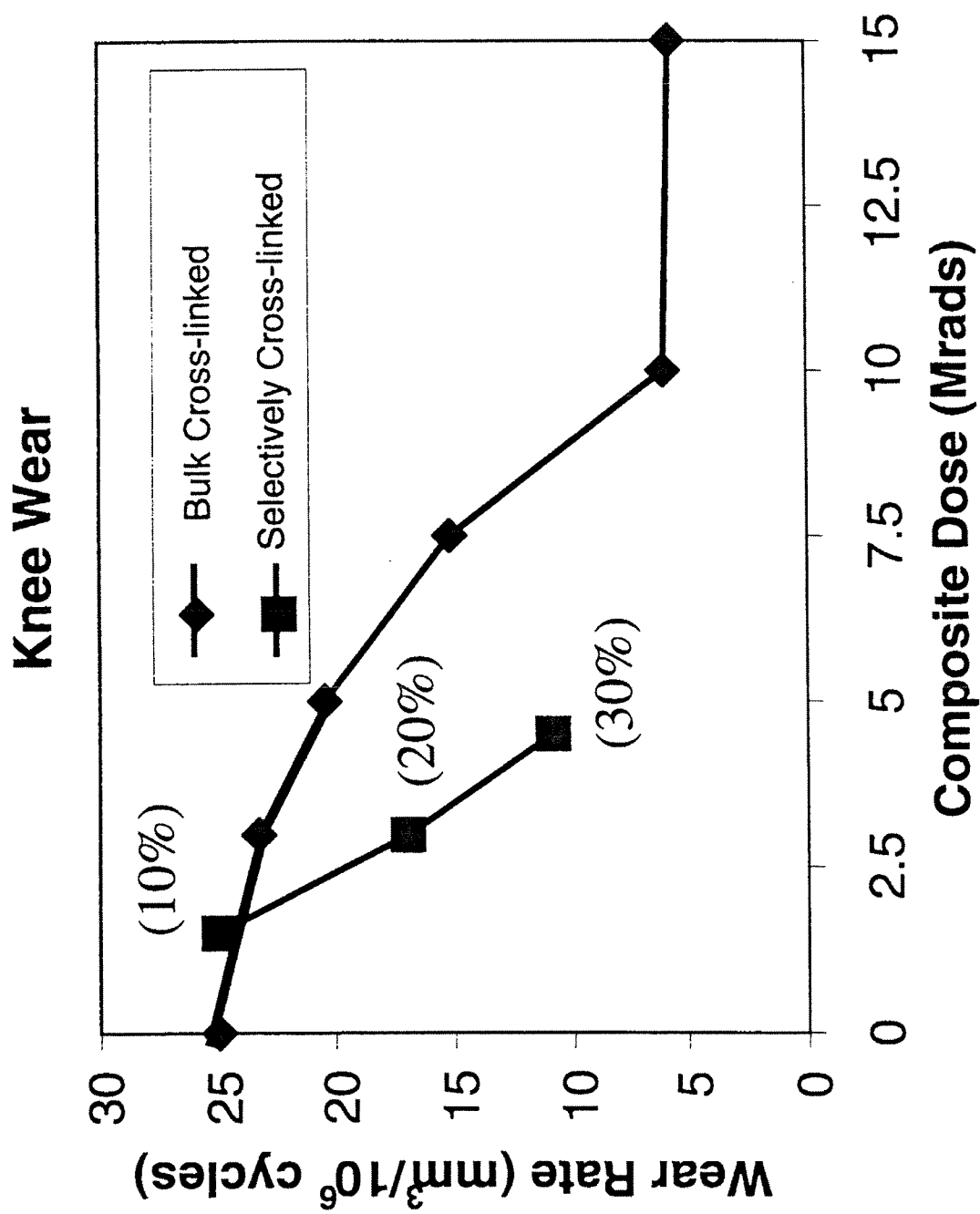


FIG. 7

Manufacturing Process

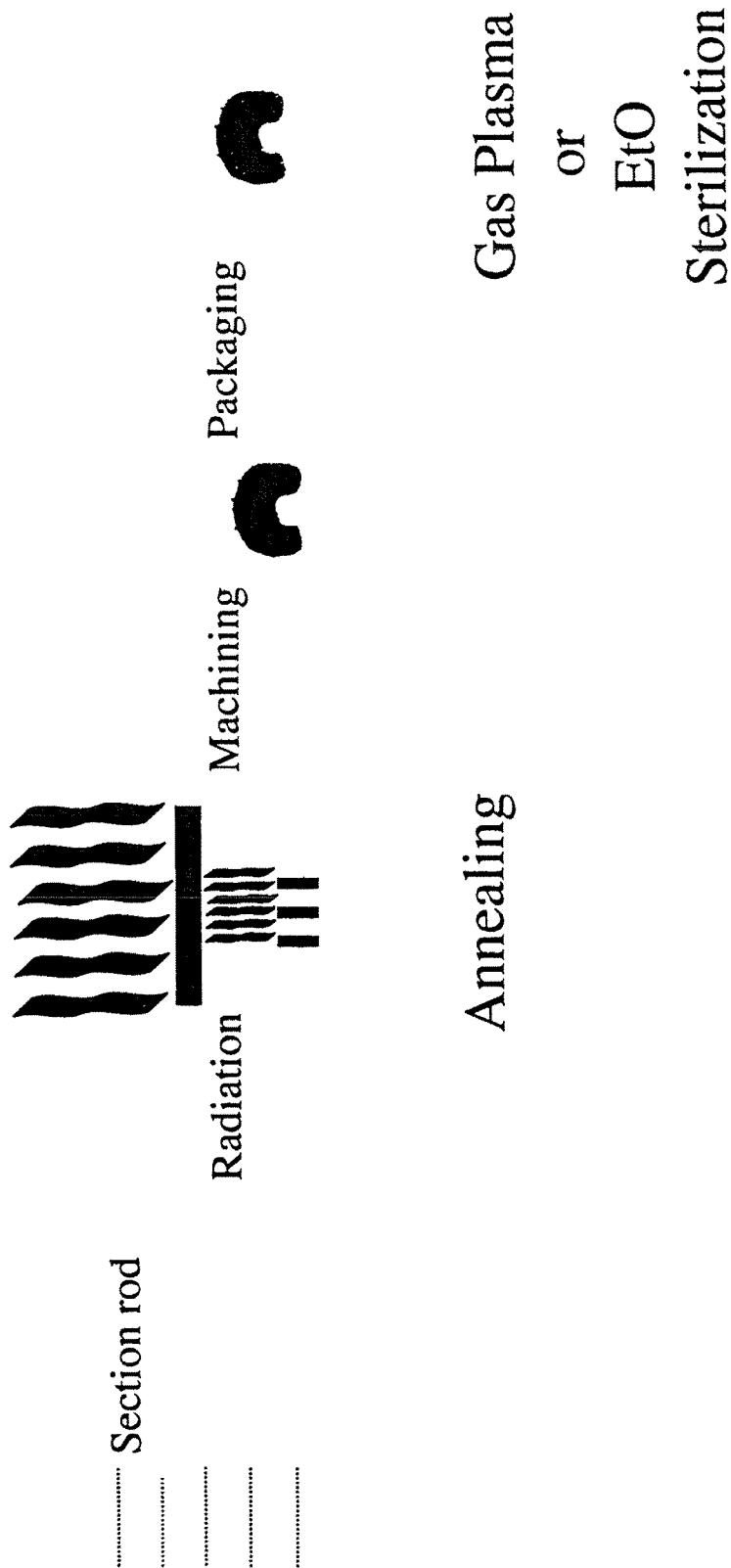


FIG. 8

Selective Crosslinking

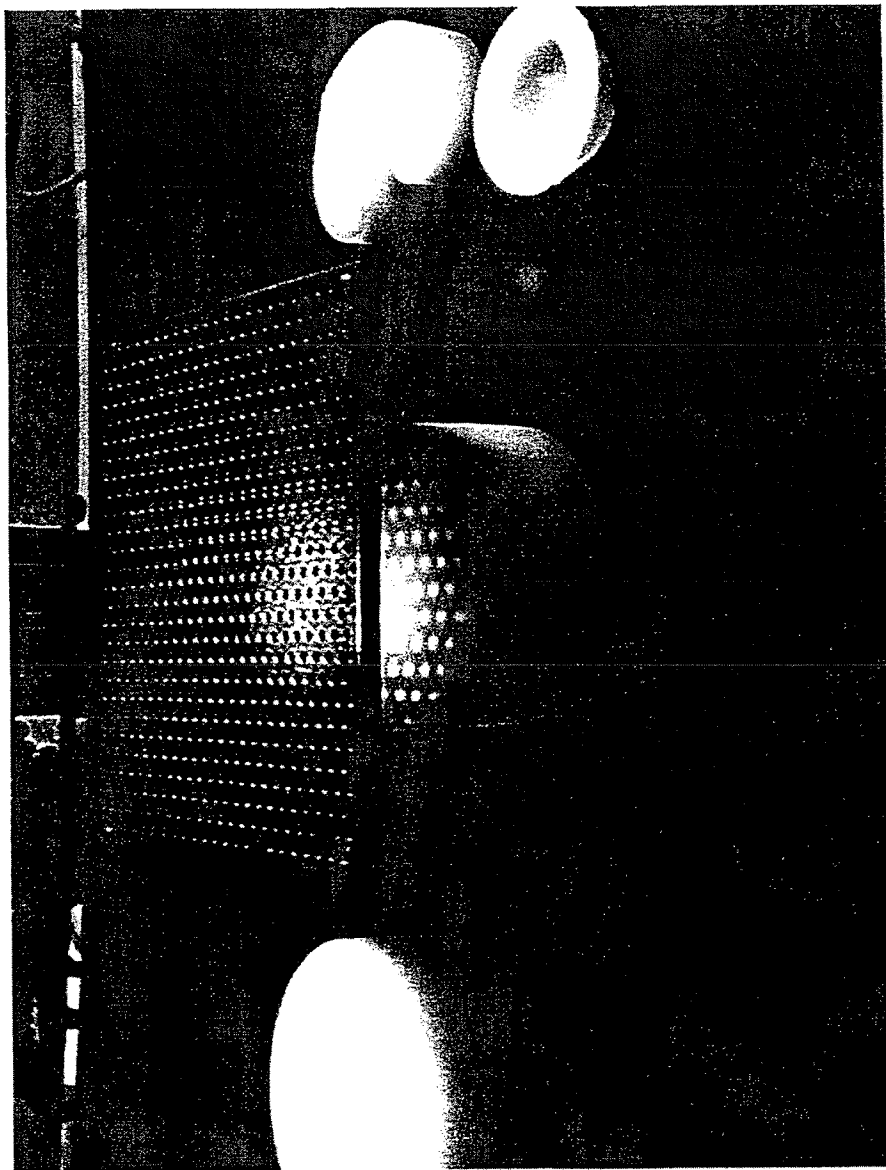
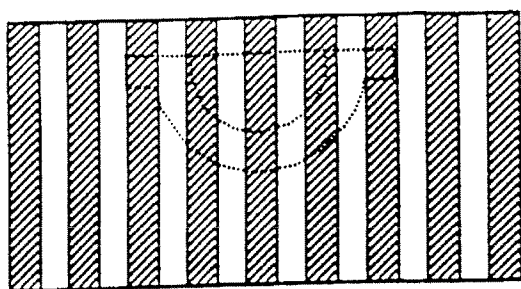
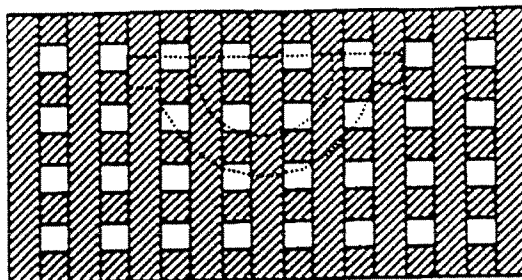


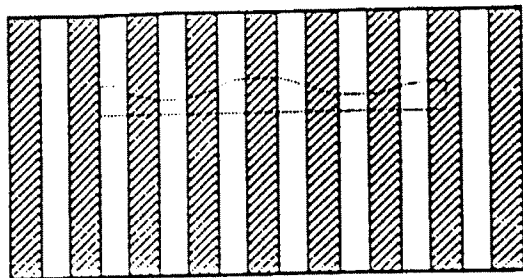
FIG.9



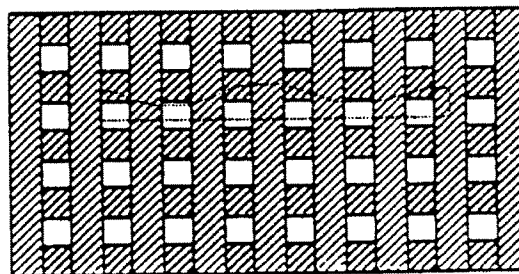
Cup



Cup



Knee



Knee

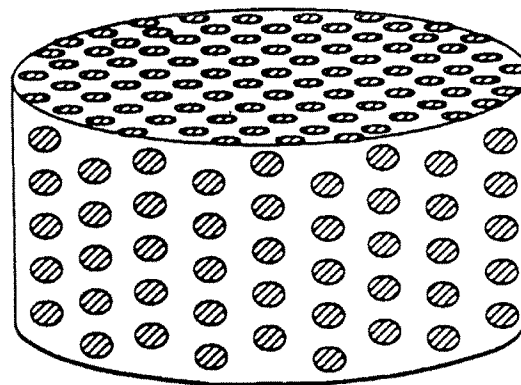
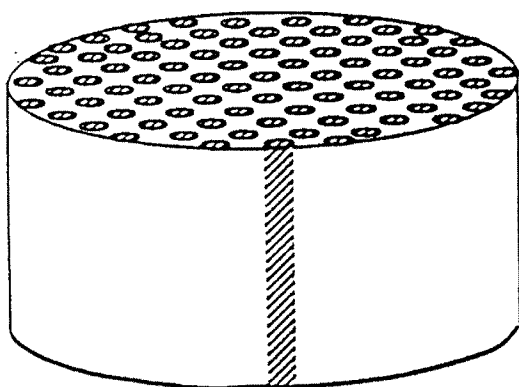


FIG. 10

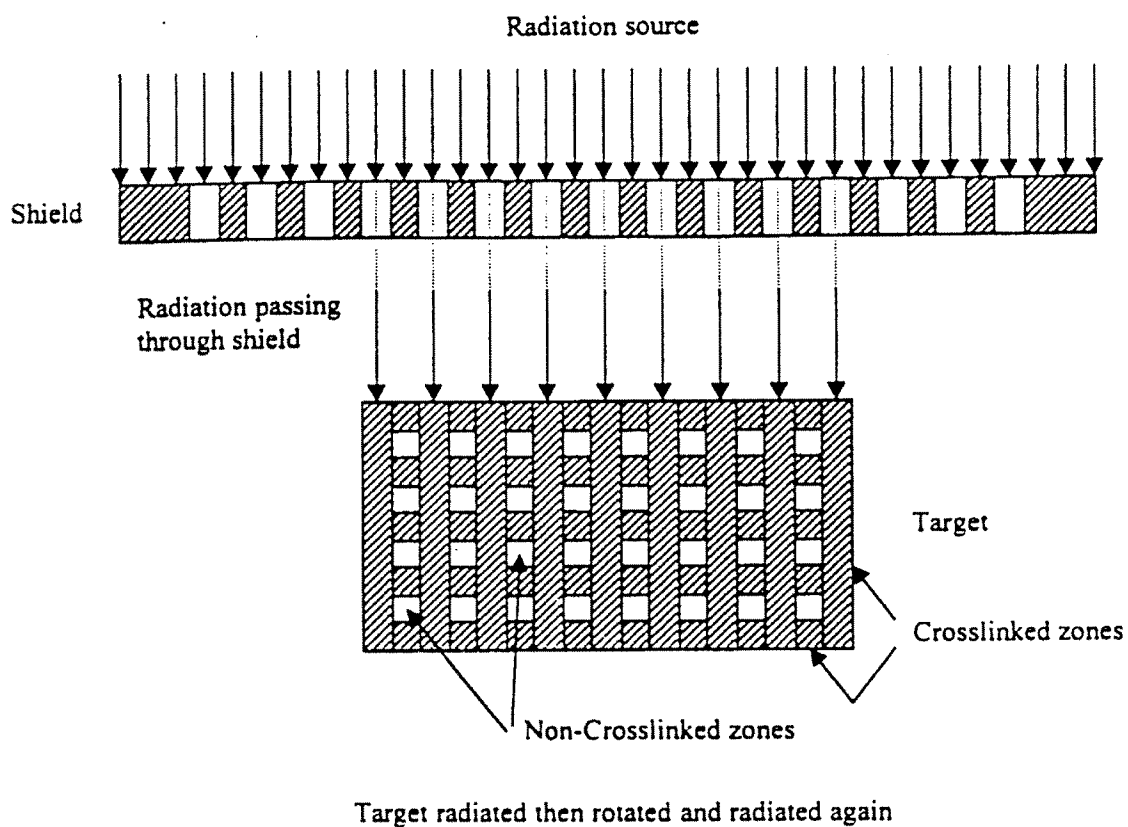


FIG. 11

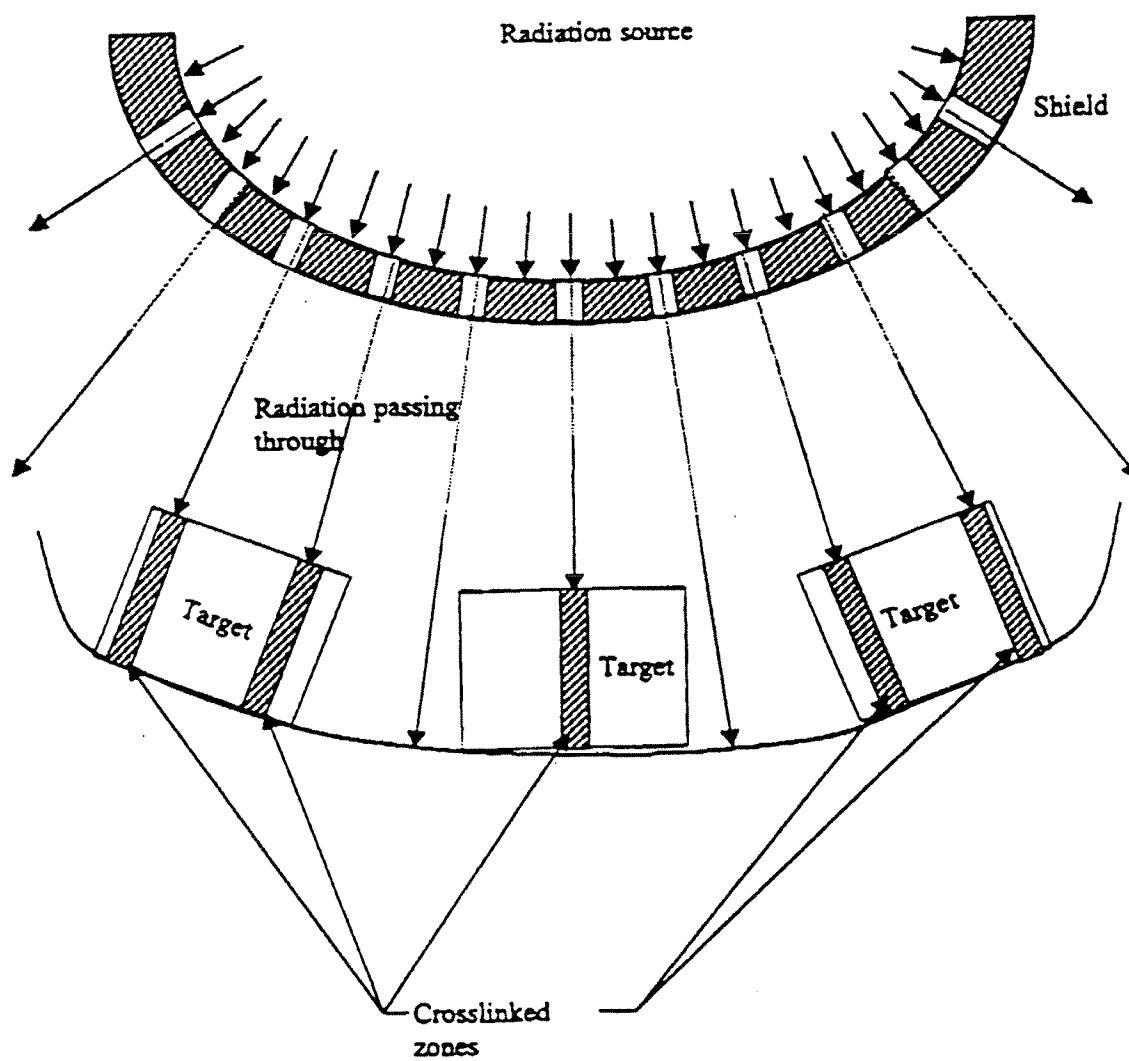


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/10673

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :A61F 2/30

US CL :623/23.58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 250/492.3; 623/22, 11, 23.24, 23.58, 901, 923, 926

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, BRS

Search Terms: crosslink\$ same (uhmwpe or hdpe or pe or polyethylene) same (irradiat\$ or radiat\$)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,832,827 A (LEMELSON) 03 September 1974, entire document, especially column 9 lines 8-25.	1, 2, 16, 30, 32, 36-39, 43-45.
A	US 5,814,423 A (MARUYAMA et al.) 29 September 1998, entire document.	1-29, 36, 37
Y	US 5,879,400 A (MERRILL et al.) 09 March 1999, entire document, especially col. 7 lines 3-17.	60

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 JULY 2000

Date of mailing of the international search report

27 JUL 2000

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Filed on	2 October 1996 (02.10.1996)
US	08/600,744 (CON)
Filed on	13 February 1996 (13.02.1996)
US	08/798,638 (CON)
Filed on	11 February 1997 (11.02.1997)

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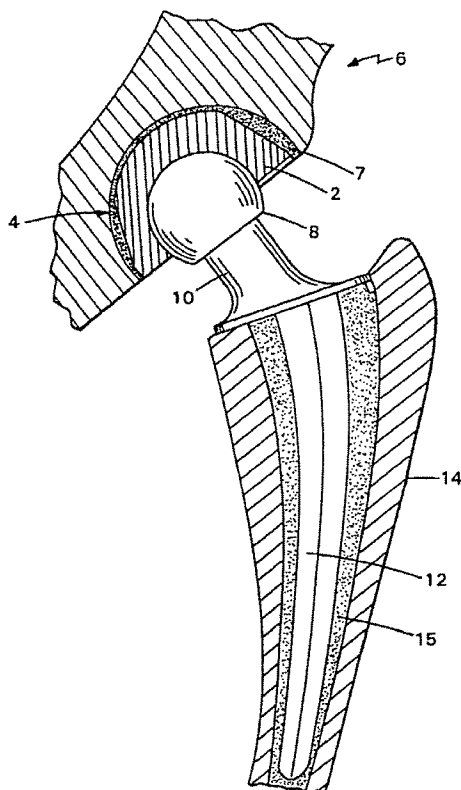
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[Continued on next page]

(54) Title: POLYETHYLENE HIP JOINT PROSTHESIS WITH EXTENDED RANGE OF MOTION



(57) Abstract: A hip joint prostheses including an acetabular cup (2) mounted in the hip socket (4) of the pelvis (6) is disclosed. The prosthesis also includes a head (8) which has a radius of curvature complementary to the cavity in the acetabular cup (2). The head (8) is typically made of metal. A neck (10) is connected to the head (8) joining the head (8) to the stem (12). The head (8), and the acetabular cup (2) are designed to allow a great deal of angular articulation. The bearing portions can be made with radiation treated ultrahigh molecular weight polyethylene polymer having substantially no detectable free radicals.

WO 01/05337 A1



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BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

- 1 -

POLYETHYLENE HIP JOINT PROSTHESIS WITH
EXTENDED RANGE OF MOTION

5 Cross Reference To Related Applications

 This is a continuation-in-part of USSN 08/798,638,
filed February 11, 1997, which is a continuation-in-part
of USSN 08/726,313, filed October 2, 1996, which is a
continuation-in-part of USSN 08/600,744, filed February
10 13, 1996, now U.S. 5,879,400. The entire contents of
each of these cases is incorporated herein by reference.

Field of the Invention

 This invention relates to hip joint prostheses.

Background of the Invention

15 Hip joint prostheses typically have a ball joint
design that includes a cup-shaped bearing portion, called
the acetabular cup, and a mating portion, which is
typically a ball-shaped element, called the head. The
head is articulated in the cavity of the cup to permit
20 motion. In a full replacement hip joint prosthesis, the
head is provided by removing the existing femur ball and
implanting a prosthetic head with a rod-like member,
known as the neck and stem, which is attached to the
femur. In another design, known as a surface replacement
25 prosthesis, the head is provided by resurfacing the
existing femur ball with a covering, typically metal.

 The cavity of the acetabular cup is typically
defined by a layer of ultra-high molecular weight
polyethylene polymer, called the polyethylene cup. The
30 useful lifetime of the prosthesis is affected by wear of
the polymer. One mechanism of wear is abrasion caused by
the motion of the head. This abrasion can liberate fine
particles which initiates biological processes ultimately

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leading to failure of the prosthesis. The failure mechanism is described further in USSN 08/798,638, incorporated, supra.

The rate of wear is influenced by the size of the head and the thickness of the polyethylene cup. As the diameter of the head increases, the distance the head slides over the polyethylene cup for a given motion, known as distance travelled, also increases, which results in greater abrasional interaction between the head and polyethylene cup, which increases wear.

The polyethylene cup thickness affects wear rate because of contact stresses, which are related to the cushioning effect of the polyethylene cup when the head bears upon it. High contact stress increases wear. Contact stress increases as polyethylene cup thickness is reduced.

As a result of these phenomena, most standard hip joint prostheses using conventional polyethylene polymer cups have a head diameter of about 32 mm or less, typically about 22 mm or 28 mm, and polyethylene cup thicknesses of about 6 mm or more. While these dimensions can provide a reasonable prosthesis lifetime, e.g., a 10% failure rate in ten years, they can also compromise performance. For example, a small head diameter reduces the range of motion and can also increase the likelihood of dislocation.

A thick polyethylene cup restricts the head size, which may be a particular problem for patients with small pelvic sockets. The head size that may be used for a given pelvic socket size is limited by the thickness of the attachment mechanism for the acetabular cup, which may include bone cement and/or a metal shell, as well as the thickness of the polyethylene cup. For example, for patients with socket diameters of about 41 mm, the most common head size is only 22 mm. The small head size can

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limit the range of motion and increase the likelihood of dislocation compared to patients with larger sockets that can accommodate larger heads.

Summary of the Invention

5 This invention relates to polyethylene hip joint prostheses that have combinations of polyethylene cup thicknesses and head diameters that can extend range of motion and also have enhanced wear resistance. The range of motion can be extended by using one or a combination
10 of a larger head size, a thin polyethylene cup, and non-hemispherical acetabular cup geometries. Wear resistance is enhanced by using an irradiated ultra-high molecular weight polyethylene polymer with substantially no detectable free radicals, a material discussed in USSN
15 08/798,638. The modulus of elasticity of this polymer can also be selected to provide greater cushioning in a thinner polyethylene cup, which reduces contact stress and the likelihood of failure modes generally, and particularly in polyethylene cups with chamfered rims.
20 In embodiments, for a given socket size, the polyethylene cup thickness is substantially reduced, which permits a substantially larger head, thus improving the range of motion and reducing the likelihood of dislocation. The lifetime of the prosthesis is extended by the wear
25 resistance and lower modulus of the polyethylene. For example, for small socket diameters of about 41 mm, the head diameter may be about 28 mm or larger. This strategy has particular advantages for patients with small sockets, typical of the Asian population, for
30 example, whose culture also involves deep flexion activities such as kneeling, e.g., in prayer, which requires extended motion range. For larger socket diameters, the invention permits head sizes that are much larger. For example, for a socket diameter of about 59

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mm, the head diameter may be about 46 mm or more. The invention also permits prostheses of the surface replacement-type in which the existing ball of the femur is capped with a metal cup and the acetabulum is fitted
5 with a thin cup of the polymer. In this case, the femur ball with the metal cup will typically have a diameter of 40 mm or more.

In one aspect, the invention features a hip joint prosthesis including a load bearing portion and a mating
10 portion that define a cavity and a head articulated to provide motion such that θ_{\max} is about 60° or more. At least one of the bearing portion and the mating portion include radiation treated ultra high molecular weight polyethylene polymer having substantially no detectable
15 free radicals. The head cross-section is greater than about 35 mm, and the thickness of the polymer is about 1 mm to about 5 mm.

In another aspect, the invention features a hip joint prosthesis including a load bearing portion and a
20 mating portion that define a cavity and a head articulated to provide motion. At least one of the bearing portion and the mating portion includes radiation treated ultra high molecular weight polyethylene polymer having substantially no detectable free radicals. The
25 head cross-section is between about 20 mm to about 35 mm and the thickness of the polymer is about 1 mm to about 5 mm.

In another aspect, the invention features a hip joint prosthesis including a load bearing portion and a
30 mating portion that define a cavity and a head articulated to provide motion. At least one of the bearing portion and the mating portion includes radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals. The thickness
35 of the polymer is about 1 mm to about 2 mm.

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In another aspect, the invention features a hip joint prosthesis including a load bearing portion and a mating portion that define a cavity and a head articulated to provide motion. At least one of the bearing portion and the mating portion includes radiation treated ultra high molecular weight polyethylene polymer having substantially no detectable free radicals. The head cross-section is greater than about 35 mm.

In still another aspect, the invention features a hip joint prosthesis system including: (a) a load bearing portion and a mating portion that define a cavity and a head articulated to provide motion, where at least one of the bearing portion and mating portion includes radiation treated ultra high molecular weight polyethylene; and (b) an attachment system for attaching the bearing portion to a patient. The attachment system includes bone cement, a metal shell, or a combination of bone cement and metal shell. The head cross-section (HS) satisfies the equation: $HS = SS - 2T_c - 2T_s - 2T_L$, where SS is pelvic socket size, T_c is bone cement thickness, which is about 0 to about 6 mm, T_s is shell thickness, which is about 0 to about 5 mm, and T_L is polymer thickness which is about 1 mm to about 5 mm. When HS is greater than about 35 mm, θ_{max} is about 60° or greater. The invention also features a kit including this system and a method of implanting a hip joint prosthesis that includes determining socket size and implanting a prosthesis of this system.

Embodiments of the invention may include one or more of the following features. The angle θ_{max} can be about 60° to about 90°, or can be about 60° to about 70°. The head cross-section can be between about 35 mm and about 40 mm, or can be between about 40 mm and about 70 mm. The thickness of the polymer can be greater than about 2 mm to about 4 mm. The thickness of the polymer

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can also be about 3 mm, about 1 mm to about 2 mm, or about 1 mm to about 4 mm.

In addition, the bearing portion can have a rim chamfer, wherein the chamfer angle θ_c is substantially equal to θ_{max} . The polymer can have a storage modulus of about 850 MPa or less. The contact stress can be less than about 10 MPa.

The cavity depth of a prosthesis can be about 16 mm or more. In addition, the bearing portion can define a sphere segment cavity and the mating portion can be a ball head. The sphere segment can be a hemisphere, or the sphere segment can define less than a hemisphere in all directions of motion. For example, the sphere segment can define less than a hemisphere in a selected direction of motion and a hemisphere in another direction of motion. The bearing portion can include the polymer and the mating portion can include metal or ceramic. In addition, the mating portion can include a prosthetic ball member attached to the femur. The mating portion can include a shell covering an existing femoral ball.

The head cross-section of a prosthesis can be about 40 mm to about 70 mm, about 20 mm to about 35 mm, or about 35 mm to about 70 mm. The head size can be about 35 mm to about 70 mm. The head cross-section (HS) can be about 28 mm or more when the pelvic socket size (SS) is about 44 mm or less. Alternatively, the head cross-section can be about 32 mm or more when the pelvic socket size is about 43 mm or more, or the head cross-section can be about 45 mm or more when the pelvic socket size is about 55 mm or more.

In the systems of the invention, T_c can be about 3 mm, T_s can be about 3.5 mm, and T_L can be about 3 to about 4 mm, for example about 3 mm. T_L can also be about 1 to about 2 mm.

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Embodiments of the invention may have one or more of the following advantages. The prostheses can provide a range of motion approaching that of a natural biological joint. For example, the range of motion for
5 the patient in the flexion/extension arc can be 120° or more, such as 120°-135°, which facilitates squatting, kneeling, bending over to tie a shoe, and the like.

As mentioned, these advantages can be beneficial in patients with small sockets because a thin
10 polyethylene cup can accommodate a larger head. The extended range of motion and improved wear characteristics can also make practical prostheses for relatively young patients, e.g., younger than age 40, and those who have an active life-style demanding greater
15 mobility. The improved wear reduces the frequency of prosthesis replacement, which minimizes the number of replacement procedures during a patient's lifetime, also an advantage for younger patients. The use of a thin polyethylene cup can also reduce the overall size of the
20 cup-head combination, which provides greater flexibility in positioning the prosthesis within the socket. The improved stability of the larger heads against partial or full dislocation reduces the need for deepening of the inner diameter of the polyethylene cup with features such
25 as countersinks, thus simplifying the prosthesis and the implant procedure and increasing the range of motion.

Still further aspects, features, and advantages follow.

Description of the Preferred Embodiments

30 We first briefly describe the drawings.

Brief Description of the Drawings

Fig. 1 is a partial cross-sectional view of a hip joint prosthesis implanted in a patient;

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Fig. 2 is a cross-sectional view of a hip joint prosthesis with a countersink;

Fig. 3 is a cross-sectional view of hip joint prosthesis having a thin polyethylene cup and a large
5 head;

Figs. 4 and 4a are expanded cross-sectional views of an polyethylene cup chamfer, illustrating the effect of increasing chamfer angle on chamfer or rim width;

Fig. 5 is a cross-sectional view of a hip joint
10 prosthesis having a large head;

Fig. 6 is a cross-sectional view of hip joint prosthesis having an acetabular cup that defines less than a hemisphere;

Fig. 7 is a cross-sectional view of a prosthesis
15 having a partially less than hemispherical cup;

Fig. 8 is a cross-sectional view of a surface-replacement hip joint prosthesis;

Fig. 9 is a cross-section through the pelvic socket illustrating selection of head size;

20 Fig. 10 is a plot of contact stress as a function of polyethylene cup thickness; and

Fig. 11 illustrates measurement of contact stress.

Description

Referring to Fig. 1, a hip joint prosthesis
25 includes an acetabular cup 2, which is mounted in the hip socket 4 of the pelvis 6. The prosthesis also includes a head 8 which has a radius of curvature complementary to the cavity in the acetabular cup. The head is typically made of metal, such as cobalt-chrome, or ceramic. A neck
30 10 is connected to the head. The neck 10 joins with a stem 12, which is connected to the femur 14 with a system 15 such as a press fit, a bone ingrowth surfacer, or cement. Alternatively, in a surface replacement prosthesis, the head could be the patient's existing

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femur ball, which is fitted with a metal or polymer cup.

The acetabular cup 2 is attached to the pelvis using an attachment system 7, which may include bone cement, a porous metal shell which permits bone ingrowth, 5 or a combination of the cement and shell. Alternatively a friction fit attachment system may be used.

Referring as well to Fig. 2, a prosthesis has a polyethylene cup 16 made of ultrahigh molecular weight polyethylene of thickness T_L . The polyethylene cup 16 has 10 an outer diameter OD_L and defines a hemispherical cavity with an internal diameter ID_L . A head 18 has, in the case of a hemispherical cup, a corresponding head cross-section diameter OD_H . The neck 20 is an elliptical or trapezoidal rod of metal or ceramic that has a maximum 15 cross section of typically about 10 mm or more.

The polyethylene cup 16 also defines a cavity depth d_c , which in the case of a hemispherical polyethylene cup, corresponds to one half the inner diameter ID_L . To reduce the likelihood of dislocation, a 20 countersink 22, is sometimes provided to increase the effective cavity depth to $d_{c'}$. The countersink is a cylindrical section of the polyethylene cup extending beyond the point at which the internal diameter of the polyethylene cup defines a hemisphere. The countersink 25 has a chamfer 24 around its rim where the neck may engage it. The angle of the chamfer is selected in coordination with the head diameter and the neck size and geometry so that the chamfer is generally parallel with the neck at θ_{max} , the maximum angular motion of the prosthesis.

30 As evident in Fig. 2, the maximum angle θ_{max} is determined when the neck 20 attached to the head 18 engages a portion of the cup, in this example, the chamfer 24 on countersink 22. As a result, the maximum motion for the prosthesis is $2\theta_{max}$.

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Referring to Fig. 3, an extended motion prosthesis 30 has a polyethylene cup 32 defining an outer diameter OD_{LE} which is the same as the polyethylene cup in Fig. 2, but has a much reduced thickness T_{LE} , thus providing a
5 larger internal diameter ID_{LE} . The larger cavity provides a larger hemispherical cavity depth, d_{CE} , which reduces the likelihood of dislocation without the need for a countersink (although one may be optionally used), and accepts a larger head 34, of diameter OD_H , which increases
10 the range of motion θ_{max} .

The polyethylene cup thickness is preferably about 1 mm to about 5 mm, or about 1 mm to about 2 mm, or about 3 mm to about 4 mm, most preferably around 3 mm. The head diameter may be larger than conventional heads or
15 provide for a patient with a small socket, a head of conventional size but still larger than typical for a given attachment system. For large heads, the head diameter may be, e.g., greater than about 35 mm, preferably in the range of about 36 mm to about 70 mm,
20 more preferably about 36 mm to about 40 mm or about 40 mm to about 70 mm. The cavity depth, d_{CE} , is preferably about 16 to about 40 mm. The maximum range of prosthesis motion, θ_{max} , is about 60° or greater, preferably about 60 to about 90°, preferably greater than about 62°, and more
25 preferably from 60-70°. The angle θ_{max} provides a total possible range of motion in an arc of $2\theta_{max}$, which is preferably about 125° to about 135°.

Referring to Fig. 4, the effect of extended θ_{max} of chamfer angle is illustrated. As mentioned, the chamfer
30 40 is the portion of the rim of the polyethylene cup that is beveled at an angle θ_c so that it is substantially parallel with the neck surface to support the neck when the prosthesis is at maximum extension. Chamfer angle θ_c is substantially equal to θ_{max} which provides a
35 substantial material width, such as the rim width, w_r , so

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that the stress on the rim of the polyethylene cup is distributed over a wide rim region.

Referring to Fig. 4a, the chamfer angle θ_c increases as θ_{max} increases, producing greater force on the rim because the chamfer width decreases. As the thickness of the polyethylene cup decreases, force on the rim increases further still.

The prostheses described herein can utilize large heads and thin polyethylene cups because they employ highly wear resistant polyethylene material for the polyethylene cup, the head, or both. A wear resistant material permits a long prosthesis lifetime even under the extended distance-travelled effect of large heads. In addition, the wear effects, particularly at the chamfer and in thin layers of polyethylene, can be reduced by modifying the material so that it has a lower modulus of elasticity.

Wear resistant polyethylene materials that can be used in the prostheses described herein are discussed in USSN 08/798,638, in WO 97/29793, and in U.S. 5,879,400. Briefly, the material is radiation treated ultra high molecular weight polyethylene having substantially no detectable free radicals. By substantially no detectable free radicals is meant substantially no free radicals as measured by electron paramagnetic resonance, as described in Jahan et al., J. Biomedical Materials Research 25:1005 (1991), the entire contents of which is incorporated herein by reference.

Free radicals include, e.g., unsaturated trans-vinylene free radicals. Ultra-high molecular weight polyethylene that has been irradiated below its melting point with ionizing radiation contains cross-links as well as long-lived trapped free radicals. These free radicals react with oxygen over the long-term and result in the embrittlement of the ultra-high molecular weight

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polyethylene through oxidative degradation. An advantage of the ultra-high molecular weight polyethylene and medical prostheses of this invention is that radiation treated ultra-high molecular weight polyethylene is used which has no detectable free radicals. The free radicals can be eliminated by any method which gives this result, e.g., by heating the ultra-high molecular weight polyethylene above its melting point such that substantially no residual crystalline structure remains. By eliminating the crystalline structure temporarily by melting, the free radicals are able to recombine and thus are eliminated. The ultra-high molecular weight polyethylene which is used in this invention has a cross-linked structure. An advantage of having a cross-linked structure is that it will reduce production of particles from the prosthesis during abrasion by the head.

For the prostheses described herein, this wear resistant polyethylene may also have a relatively low modulus of elasticity, which increases cushioning effect even in thin polyethylene cup, thus reducing contact stress generally, and particularly at the chamfer. Referring to Fig. 10, a plot of contact stress as a function of thickness illustrates that, for conventional polyethylene (UHMPE), contact stress increases quickly at small polyethylene cups thickness compared to the wear resistant radiation treated ultra-high molecular weight polyethylene, for which contact stresses are less at all levels. Preferably, for these prostheses, the storage modulus of elasticity is about 850 MPa or less, e.g. between about 100-800 MPa. The contact stress is preferably about 17 MPa for small sockets and 10 MPa for larger sockets. (Measurement of contact stress and storage modulus are discussed infra.)

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The modulus of elasticity can be modified by varying the radiation treatment during manufacture of the polymer. Several techniques for manufacture of the polyethylene are provided in USSN 08/798,638. These
5 include cold irradiation and subsequent melting (CIR-SM), warm irradiation and subsequent melting (WIR-SM), warm irradiation adiabatic melting (WIR-AM or WIAM), and melt irradiation (MIR). Generally, in MIR, modulus of elasticity decreases with dose level. In WIR-AM and CIR-
10 SM, after an initial decrease, the modulus is constant to about 15 Mrad but then declines at higher doses. Crystallinity level may be used as an indicator of modulus. Crystallinity as a function of dose is described in WO 97/29793 (see, e.g., Fig. 4).

15 Additional Embodiments

Referring now to Fig. 5, an extended motion prosthesis 50 has a polyethylene cup 52 of thickness T_L similar to conventional cup thickness, but defines a hemispherical cavity having an inner diameter of ID_{LE} ,
20 much larger than the conventional prosthesis to accept a large head of corresponding outer diameter. As evident, the larger head and greater cavity depth d_{CE} reduce the likelihood of dislocation without the need for an extension cylinder and increase range of motion θ_{max} . The
25 polyethylene cups thickness in this case may be, e.g., about 6 to 8 mm. The ball diameter and range of motion may be as described above. As discussed above, the wear resistance of the irradiated ultra high molecular weight polyethylene having substantially detectable no free
30 radicals withstands the distance travelled wear effect of the larger head.

Extended motion prostheses using large heads and/or thin polyethylene cups can also be implemented with non-hemispherical geometries. Referring to Fig. 6,

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a prosthesis 60 with a less than hemispherical polyethylene cup 62 is illustrated. The polyethylene cup 62 defines a large internal diameter ID_L to accommodate a large diameter head 64. The polyethylene cup does not
5 extend to a full hemisphere but rather defines a sphere segment extending only to an angle α , defined between the center of the arc and the rim of the polyethylene cup. As evident, the sphere segment provides an extended motion compared to a hemisphere. In addition, the
10 polyethylene cup provides a large cavity depth d_{CE} to reduce the likelihood of dislocation.

The relationship between the cavity depth and the angle α can be expressed as:

$$d_{CE} = \frac{ID_E}{2} (1 - \sin \alpha)$$

The angle α is preferably between about 1-45°,
15 more preferably between about 10-20°. The head diameter, polyethylene cup thickness, and cavity depths are preferably in the ranges given above. As discussed above, the wear resistance of the irradiated ultra high molecular weight polyethylene having substantially
20 detectable no free radicals withstands the distance travelled wear effect of the larger head and thin polyethylene cups.

Referring to Fig. 7, in another embodiment, an extended motion prosthesis 70 has an polyethylene cup 72
25 that is non-hemispherical only in certain directions of motion. In this example, the polyethylene cup is substantially hemispherical in the direction of adductive motion, where a large range of motion does not normally occur, but is less than hemispherical in the direction of
30 flexion/extension. The non-hemispherical portion 74 appears as a cut-out region in the body of the polyethylene cup. The angle of the cut out may be in the

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range of α , discussed above. The head diameter and polyethylene cup thickness are preferably in the ranges given above. As discussed above, the wear resistance of the irradiated ultra high molecular weight polyethylene
5 having substantially detectable no free radicals withstands the distance travelled wear effect of the larger head.

Referring to Fig. 8, a thin polyethylene cup and large head can be used in surface replacement prostheses.
10 In this case, the existing ball 82 on the femur 84 is covered with a femur cup 86 and the acetabulum is provided with a thin acetabular cup 90. The ball with the femur cup may be relatively large, with a diameter approaching or even exceeding the normal femur ball
15 diameter. The acetabular cup and the ball cup are preferably thin, e.g. around 1 mm to 5 mm, preferably about 1 mm to about 2 mm, preferably about 3 mm. Either the acetabular cup or the ball cup may be formed of polymer, with the mating component made of metal or
20 ceramic (e.g. 3 mm thick), or both cups may be polymer. The wear resistant polymer permits a large diameter ball and thin polymer layers without excessive wear.

In any of the embodiments, the thickness of the cup can also vary in the direction of different motions.
25 For example, the cup may be thicker where greater wear is likely. Extended motion can still be achieved in spite of the thicker polyethylene cup by, e.g., implementing a less than hemispherical geometry or a much larger head hemispherical geometry.

30 In some embodiments, the head may also comprise the wear resistant polymer. The polymer may be provided as a thin covering or cup over a metal ball, or the entire ball may be made of polymer. In cases where the ball includes polymer, the acetabular cup may be metal,
35 without a polymer cup.

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The head is preferably spherical but may alternatively be nonspheroid, for example, the head may be ovaloid. The term head diameter or head size (HS) refers to the effective diameter determined by twice the
5 radius of curvature of the head. For non-spheroid heads the cross section refers to the largest cross section.

Selection of Prostheses Parameters

The ultimate size of the head that may be implemented in a patient is determined in part by the
10 method of attachment. Using a prosthesis with a thin polyethylene cup, as discussed above, can increase flexibility in terms of attachment technique because the overall diametric cross section of the acetabular cup and head combination will be reduced.

15 Generally, the prosthesis may be fixed to the patient's socket by several of known techniques, such as those using bone cement (e.g., methylmethacrylate), bone ingrowth, press-fit, screws, spikes, or a metal mesh embedded in polyethylene, as described, e.g., in Morscher
20 et al., Clinical Orthopaedics and Related Research, No. 341, pp. 42-50 (1997). Metal shell and metal mesh systems may be used. The systems may be modular (e.g., the Trilogy System available from Zimmer, Warsaw, IN), in which case the components are implanted sequentially, or
25 they may be a preassembled unit (e.g., the Sulmesh system, available from Sulzer Orthopedics, Baar, Switzerland).

Referring to Fig. 9, the physician determines the size of the hip socket 80, e.g., by direct observation
30 during surgery, and delivers the most appropriate attachment system. As illustrated, a socket size SS may be occupied by cement 82 of thickness T_c , a shell or mesh 84 of thickness T_s , a polyethylene cup 86 of thickness T_L and a head 88 of size HS. In some cases, no shell is

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used and in others, no cement is used. (Additionally a layer of cement between the cup and shell may also be used.)

The head size is calculated as follows:

$$5 \quad HS = SS - 2T_c - 2T_s - 2T_L$$

Preferably, the cup thickness may be about 1 mm to about 5 mm, most preferably about 3 mm. The shell or mesh thickness, when used, is about 1 mm to about 5 mm, preferably about 3 mm to about 4 mm. The cement
10 thickness is about 1 mm to about 6 mm, typically 2-3 mm.

Table I illustrates examples of treatment of very small (41 mm), small (45 mm) and mid size (59 mm) socket sizes, using direct attachment of the polyethylene cup without cement.

15 TABLE I

	Very Small Socket	Small Socket	Mid size Socket
SS	41 mm	45 mm	59 mm
T_s	3.5 mm	3.5 mm	3.5 mm
T_L	3.0 mm	3.0 mm	3.0 mm
HS	28 mm	32 mm	46 mm

20 For a patient with a very small socket, the head size is 28 mm, for a patient with a small socket, the head size is 32 mm, and for a patient with a midsize socket, the head size is 46 mm.

Measurement of Storage Modulus

25 A dynamic mechanical analyzer is used to measure the storage (in-phase modulus) as a function of frequency and temperature. The control ultra-high molecular weight polyethylene (UHMWPE) used in this example was GUR 1050

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ram extruded bar stock available from PolyHi Solidur, Ft. Wayne, IN. Three test samples (~3.2 mm wide; ~1.3 mm thick; 25 mm long) were machined using a milling machine. The test samples were subsequently sterilized with gamma radiation in an oxygenless packaging.

The irradiated material was WIAM-TREATED GUR 1050 ram extruded bar stock. To prepare this material, polyethylene was preheated to 125°C, irradiated with a 10 MeV electron beam (Impela 10-50, E-Beam Services, Cranbury, NJ) to a total dose level of 9.5 Mrad at a conveyor speed of 13.2 inches/minutes with a scan length of 32 inches. The samples were subsequently melt-annealed at 150°C for two hours.

The test samples (~3.2 mm wide; ~1.3 mm thick; 25 mm long) were machined from the center of the irradiated hockey puck. The test samples were subsequently sterilized with ethylene oxide gas.

A Perkin Elmer Dynamic Mechanical Analyzer-7 (DMA-7) was used to measure the in-phase modulus of the control and WIAM-treated UHMWPE in 3-point bending. The DMA-7 was calibrated for the height, force, temperature, and furnace parameters following the instructions of the manufacturer. A reference material, epoxy of known modulus (~1.1 GPa), was used to validate the measured values of the in-phase modulus. The measured storage modulus of the reference epoxy is shown in the following table as a function of frequency.

TABLE II

1Hz	2Hz	3Hz	4Hz	5Hz	6Hz	7Hz	8Hz	9Hz	10Hz
1.105	1.105	1.108	1.106	1.109	1.107	1.111	1.111	1.111	1.108
GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa

Three test samples of each series were used to measure the in-phase and out-of-phase moduli at a temperature of 25° C and at frequencies of 1 and 2 Hz.

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higher for both: 873 ± 37 MPa for control and 676 ± 30 MPa for WIAM.

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Table III: Elastic modulus values measured for the control and WIAM treated UHMWPE. The static load was 100 mN and the dynamic load was 80 mN.

Sample ID	Frequency (Hz)	Storage Modulus (MPa)	Loss Modulus (MPa)	Tan (δ)	Phase angle	Static stress (MPa)	Dynamic stress (MPa)	Total stress (MPa)	Amplitude (μm)
Control 1	1	832	64	0.07	4.4	0.53	0.42	0.95	26
Control 2	1	830	59	0.07	4.2	0.35	0.38	0.73	14
Control 3	1	905	64	0.07	4.0	0.35	0.28	0.63	13
Average		855 \pm 42	62 \pm 2.9	0.07	4.2 \pm 0.2				
Control 1	2	852	53	0.06	3.5	0.53	0.43	0.96	26
Control 2	2	851	47	0.06	3.0	0.35	0.28	0.63	14
Control 3	2	917	52	0.06	3.2	0.35	0.28	0.63	13
Average		873 \pm 37	51 \pm 3.2	0.06	3.2 \pm 0.5				
WIAM 1	1	653	69	0.1	6.1	0.56	0.44	1.00	37
WIAM 2	1	623	64	0.1	5.9	0.33	0.26	0.59	16
WIAM 3	1	695	62	0.1	5.1	0.36	0.29	0.65	17
Average		657 \pm 36	6.5 \pm 3.6	0.1	5.7 \pm 0.5				
WIAM 1	2	675	59	0.08	5.0	0.57	0.45	1.02	35
WIAM 2	2	546	55	0.08	4.8	0.33	0.26	0.59	16
WIAM 3	2	707	54	0.07	4.4	0.37	0.29	0.66	17
Average		676 \pm 30	56 \pm 2.6	0.08	4.7 \pm 0.3				

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Measurement of Contact Stress

Referring to Fig. 11, contact stress is measured by observing color change in a stress sensitive film disposed between a head and a cup arranged in a hydraulic testing machine. The Fuji Prescale Film (Medium Mono Sheet Type film, available from Sensors Products, Inc., E. Hanover, NJ) changes color under stress. The intensity of the color change on the film is proportional to the applied stress. A stress chart provided with the Fuji Prescale Film can then be used to determine the applied stress. An example of this measurement follows.

Fuji Film Prescale was used to quantify the contact stress between the cobalt-chrome femoral heads and control and WIAM-treated ultra-high molecular weight polyethylene liners. The Fuji film used was the medium pressure film with a stress range of 10-50 MPa (1422-7110 psi).

The following liners (i.e., polyethylene cups) were used to determine the contact stresses:

1. WIAM liners with 22 mm inner diameter and 39 mm outer diameter.
2. WIAM liners with 28 mm inner diameter and 49 mm outer diameter.
3. WIAM liners with 32 mm inner diameter and 55 mm outer diameter.
4. Control liners with 22 mm inner diameter and 39 mm outer diameter.
5. Control liners with 26 mm inner diameter and 49 mm outer diameter.
6. Control liners with 28 mm inner diameter and 49 mm outer diameter.
7. Control liners with 32 mm inner diameter and 55 mm outer diameter.

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The WIAM liners used were made of DuraSul, available from Sulzer Orthopedics. The control liners used were InterOp acetabular liners, also available from Sulzer.

5 A 3 mm thin strip of Fuji Prescale Film was placed between the femoral head and the corresponding liner. The components were then loaded on an MTS servo hydraulic testing machine (MTS 810 Test System, available from MTS Systems Corp., Eden Prairie, MN) to a load of 2670N (600
10 lbs). Each load was applied for a duration of two minutes as recommended for the use of Fuji Prescale Film. The thin strip was then removed and the color change was analyzed using the stress chart provided with the fuji Prescale Film. The darkest region in each strip was
15 analyzed with the color-coded stress chart. Therefore, the contact stress values reported here are the maximum encountered during loading. A total of three contact stress measurements were carried out for each homologous series. The contact stresses measured in each homologous
20 series are listed in Table IV.

Table IV

Sample ID	Contact stress in 22 mm inner diameter 39 mm outer diameter with 22 mm femoral head (MPa)	Contact stress in 26 mm inner diameter XX mm outer diameter with 26 mm femoral head (MPa)	Contact stress in 28 mm inner diameter 49 mm outer diameter with 28 mm femoral head (MPa)	Contact stress in 32 mm inner diameter 55 mm outer diameter with 32 mm femoral head (MPa)
Control 1	28	25	22	13
Control 2	28	25	22	13
Control 3	28	25	22	13
Average	28±0	25±0	22±0	13±0
WIAM 1	26	NA	17	10
WIAM 2	26	NA	17	10
WIAM 3	26	NA	17	10
Average	26±0	NA	17±0	10±0

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As the results indicate, the contact stresses measured for the control liners were higher than those measured for WIAM-treated liners. Based on the contact stress values obtained from the other WIAM liners, it is
5 believed that the contact stress in WIAM liners with 26 mm inner diameter and 49 mm outer diameter will be between 17 and 26 MPa. As discussed above, contact stress can be reduced by decreasing the modulus of elasticity.
10 Still further embodiments are within the following claims.

What is claimed is:

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1. A hip joint prosthesis comprising a load bearing portion and a mating portion that define a cavity and a head articulated to provide motion such that θ_{\max} is about 60° or more, wherein at least one of the bearing
5 portion and the mating portion comprises radiation treated ultra high molecular weight polyethylene polymer having substantially no detectable free radicals, wherein the head cross-section is greater than about 35 mm, and where the thickness of said polymer is about 1 mm to
10 about 5 mm.

2. The prosthesis of claim 1 wherein θ_{\max} is about 60° to about 90° .

3. The prosthesis of claim 1 wherein θ_{\max} is about 60° to about 70° .

15 4. The prosthesis of claim 1 wherein the head cross-section is between about 35 mm and about 40 mm.

5. The prosthesis of claim 1 wherein the head cross-section is about 40 mm to about 70 mm.

6. A hip joint prosthesis comprising a load
20 bearing portion and a mating portion that define a cavity and a head articulated to provide motion, wherein at least one of the bearing portion and the mating portion comprises radiation treated ultra high molecular weight polyethylene polymer having substantially no detectable
25 free radicals and wherein the head cross-section is between about 20 mm to about 35 mm and the thickness of said polymer is about 1 mm to about 5 mm.

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7. The prosthesis of claim 1 or claim 6 wherein the thickness of the polymer is greater than about 2 mm to about 4 mm.

8. The prosthesis of claim 1 or claim 6 wherein
5 the thickness is about 3 mm.

9. The prosthesis of claim 1 or claim 6 wherein the thickness is about 1 mm to about 2 mm.

10. The prosthesis of claim 1 or claim 6 wherein the bearing portion has a rim chamfer, wherein the
10 chamfer angle θ_c is substantially equal to θ_{max} .

11. The prosthesis of claim 1 or claim 6 wherein the polymer has a storage modulus of about 850 MPa or less.

12. The prosthesis of claim 1 or claim 6 wherein
15 the contact stress is less than about 10 MPa.

13. The prosthesis of claim 1 or claim 6 wherein the cavity depth is about 16 mm or more.

14. The prosthesis of claim 1 or claim 6 wherein the bearing portion defines a sphere segment cavity and
20 said mating portion is a ball head.

15. The prosthesis of claim 14 wherein the sphere segment is a hemisphere.

16. The prosthesis of claim 14 wherein the sphere segment defines less than a hemisphere in all directions
25 of motion.

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17. The prosthesis of claim 14 wherein the sphere segment defines less than a hemisphere in a selected direction of motion and a hemisphere in another direction of motion.

5 18. The prosthesis of claim 14 wherein the bearing portion comprises said polymer and the mating portion comprises metal or ceramic.

 19. The prosthesis of claim 14 wherein the mating portion comprises a prosthetic ball member attached to
10 the femur.

 20. The prosthesis of claim 14 wherein the mating portion comprises a shell covering an existing femoral ball.

 21. A hip joint prosthesis comprising a load
15 bearing portion and a mating portion that defines a cavity and a head articulated to provide motion, wherein at least one of the bearing portion and the mating portion comprises radiation treated ultra high molecular weight polyethylene having substantially no detectable
20 free radicals and the thickness of the polymer is about 1 mm to about 2 mm.

 22. The prosthesis of claim 21 wherein the head cross-section is about 40 mm to about 70 mm.

 23. The prosthesis of claim 21 wherein the head
25 cross-section is about 20 mm to about 35 mm.

 24. A hip joint prosthesis comprising a load bearing portion and a mating portion that define a cavity and a head articulated to provide motion, wherein at

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least one of the bearing portion and the mating portion comprises radiation treated ultra high molecular weight polyethylene polymer having substantially no detectable free radicals and wherein the head cross-section is
5 greater than about 35 mm.

25. The prosthesis of claim 24 wherein the head size is about 35 mm to about 70 mm.

26. A hip joint prosthesis system comprising:

(a) a load bearing portion and a mating portion
10 that define a cavity and a head articulated to provide motion wherein at least one of said bearing portion and mating portion comprises radiation treated ultra high molecular weight polyethylene; and

(b) an attachment system for attaching said
15 bearing portion to a patient, said attachment system comprising bone cement, a metal shell, or a combination of bone cement and metal shell,

wherein the head cross-section (HS) satisfies:

$$HS = SS - 2T_c - 2T_s - 2T_L$$

20 where

SS is pelvic socket size,

T_c is bone cement thickness, which is 0 to about 6
mm,

T_s is shell thickness, which is 0 to about 5 mm,

25 T_L is polymer thickness which is about 1 mm to about 5 mm, and

when HS is greater than about 35 mm, θ_{\max} is about 60° or greater.

27. The system of claim 26 wherein HS is about 28
30 mm or more when SS is about 44 mm or less.

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28. The system of claim 26 wherein HS is about 32 mm or more when SS is about 43 mm or more.

29. The system of claim 26 wherein HS is about 45 mm or more when SS is about 55 mm or more.

5 30. The system of claim 26 wherein T_c is about 3 mm.

31. The system of claim 26 wherein T_s is about 3.5 mm.

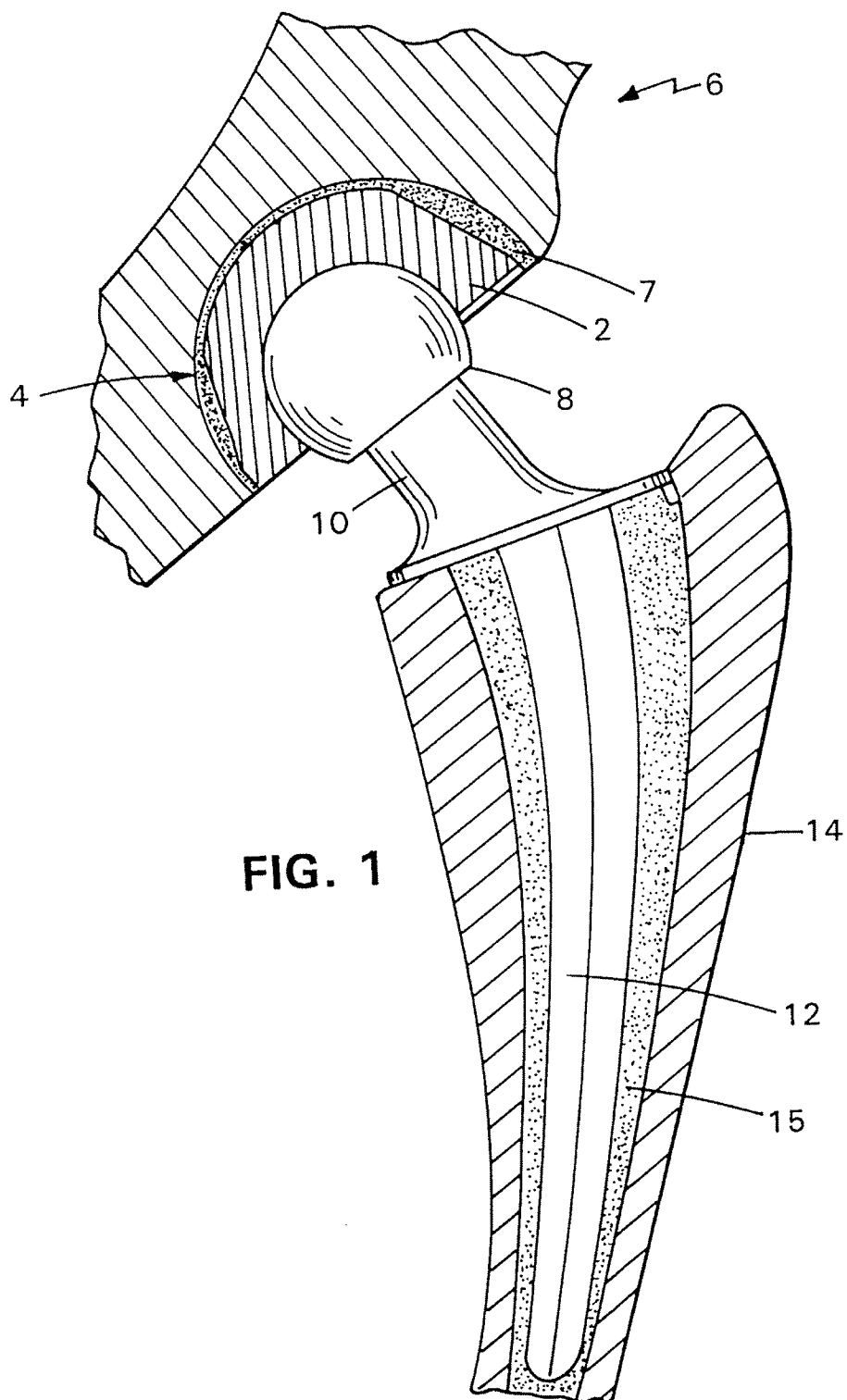
32. The method of claim 26 wherein T_L is about
10 3 to about 4 mm.

33. The method of claim 26 wherein T_L is about 3 mm.

34. The method of claim 26 wherein T_L is about 1 to about 2 mm.

15 35. A kit comprising a prosthesis system described in claim 26.

36. A method of implanting a hip joint prosthesis, comprising determining socket size, and implanting a prosthesis described in claim 26.



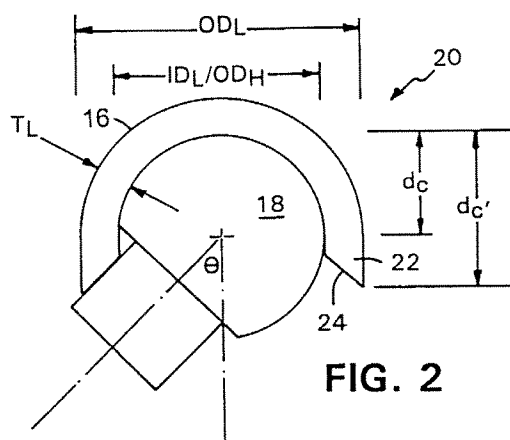


FIG. 2

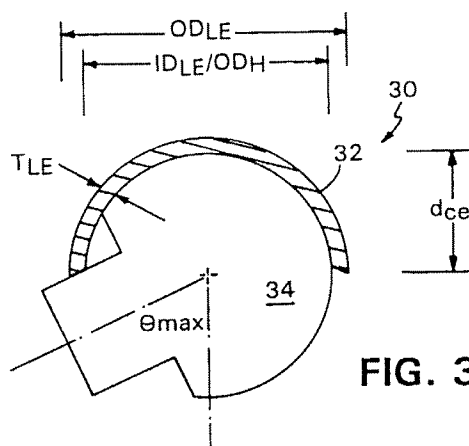


FIG. 3

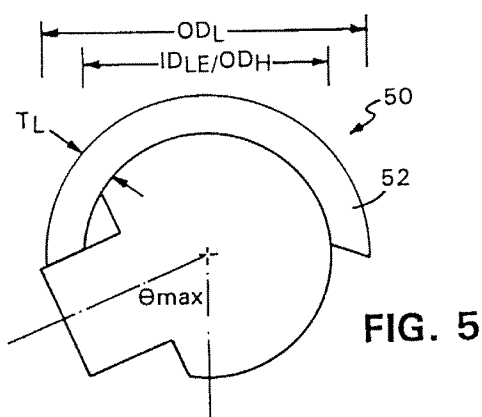


FIG. 5

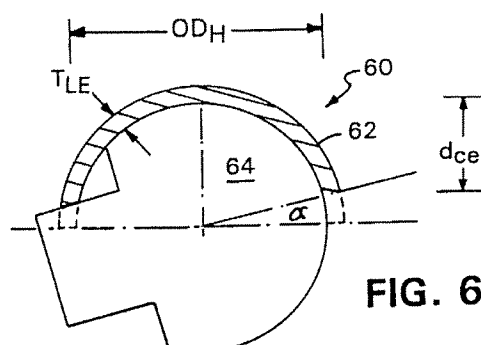


FIG. 6

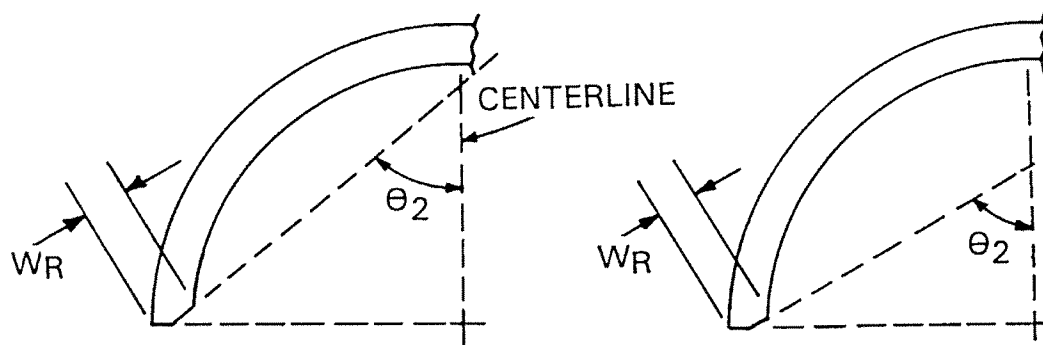


FIG. 4

FIG. 4A

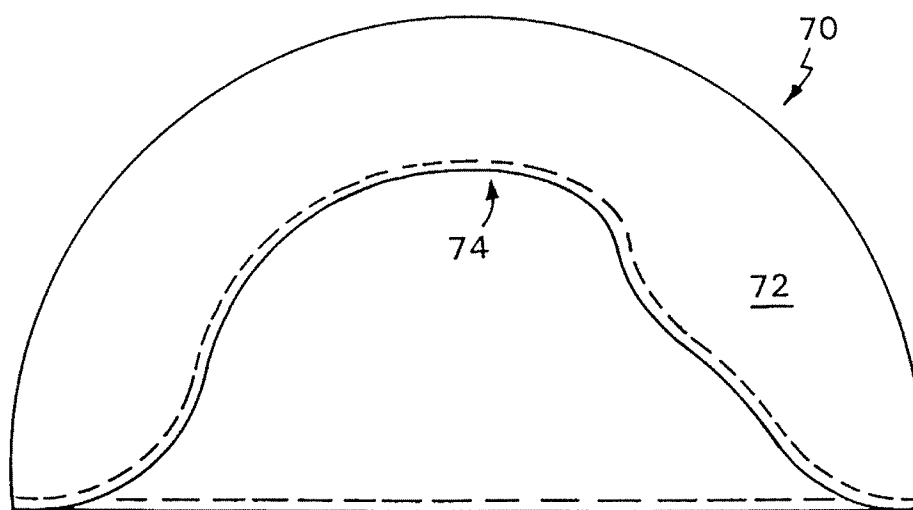
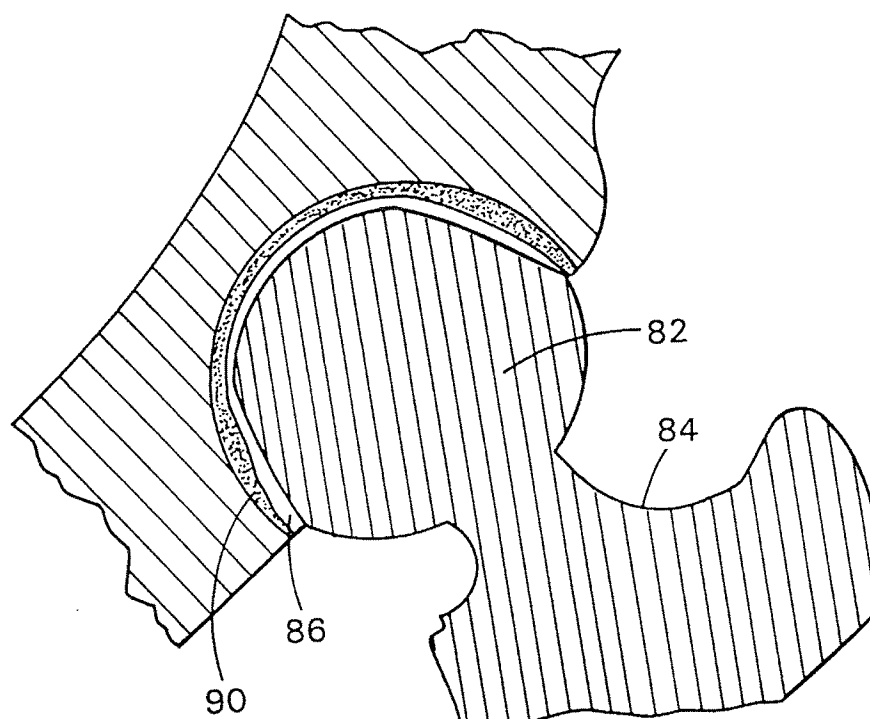
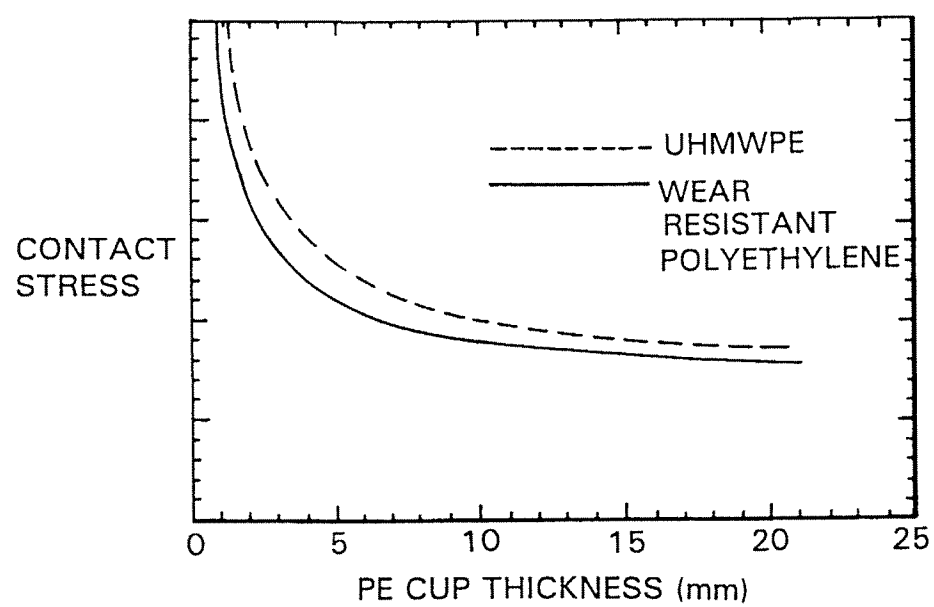


FIG. 7

**FIG. 8****FIG. 10**

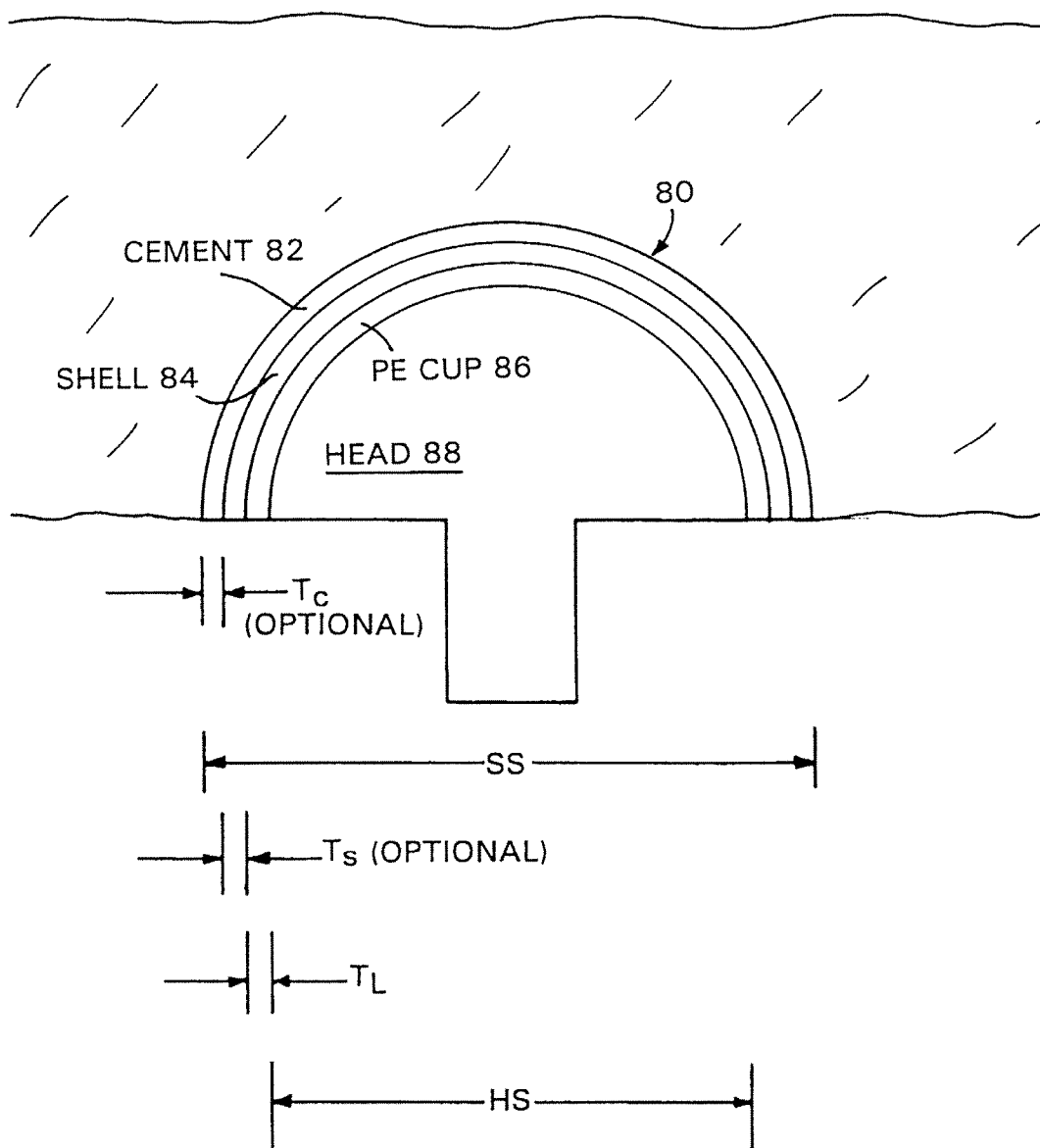
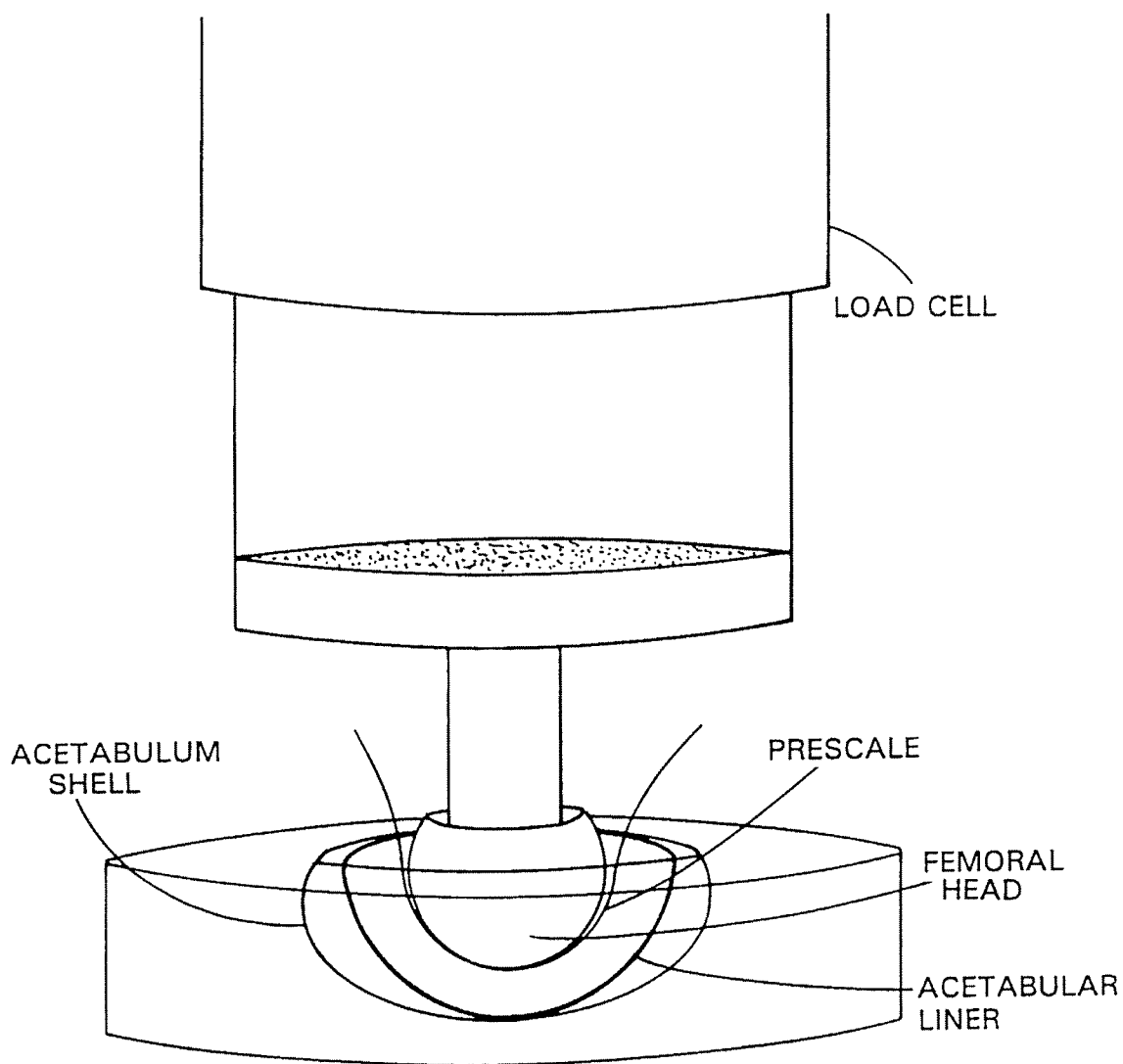


FIG. 9



CONTACT STRESS MEASUREMENTS

FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/16070

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61F 2/32

US CL :623/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/2.24, 2.26, 222, 296, 307, 308, 316, 528, 530, 534; 526/352; 623/16, 18-23

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,549,700 A (GRAHAM et al) 27 August 1996, entire document.	1-18, 20-36
A	US 4,535,486 A (ROBERTS et al) 20 August 1985, entire disclosure.	1-18, 20-36
A	US 5,593,719 A (DEARNALEY et al) 14 January 1997, entire document.	1-18, 20-36
A	STREICHER, R. M., Investigation on Sterilization and Modification of High Molecular Weight Polyethylene by Ionizing Irradiation. Reprints from beta-gamma 1/89, January 1989., 10 pages.	1-18, 20-36

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 13 SEPTEMBER 1999	Date of mailing of the international search report 20 OCT 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer PAUL PREBILIC Telephone No. (703) 308-2905